APR 21 193

Volume XXXIII April, 1932 Number 4

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

Contents

A New Type of Hydrometer for the Mechanical Analysis of Soils. AMAR NATH PURI 241

Replaceable Bases in the Soils of Southeastern Minnesota and the Effect of Lime upon Them. C. O. ROST AND JEAN M. ZETTERBERG 249

Effects of Stable Manure and Certain Fertilizers on the Microbiological Activities in Virgin Peat. S. C. VANDECAVEYE 279

The Laws of Soil Colloidal Behavior: VIII. Forms and Functions of Water. SANTE MATTSON 301

PUBLISHED MONTHLY
THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES
BALTIMORE, MARYLAND, U. S. A.

Made in United States of America

SOIL SCIENCE

FOUNDED BY
RUTGERS COLLEGE
NEW BRUNSWICK, N. J.

ADVISORY STAFF

Prof. A. W. Blair, Dr. J. S. Joffe, Prof. L. L. Lee, Dr. H. C. McLean, Dr. S. Mattson, Prof. A. L. Prince, Dr. J. W. Shive, Dr. R. L. Starkey and Dr. S. A. Waksman, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

DR. F. J. ALWAY
University of Minnesota, St. Paul, Minn.

PROF. K. ASO
Imperial University, Tokyo, Japan

PROF. C. BARTHEL
Central Agricultural Experiment Station, Experimentalfaltet, Sweden

DR. P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa

PROF. DR. ALBERT DEMOLON
Ministry of Agriculture, Paris, France

DR. H. J. CONN
New York State Experiment Station, Geneva, N. Y.

DR. E. B. FRED
University of Wisconsin, Madison, Wis.

DR. J. E. GREAVES
Utah Agricultural College, Logan, Utah

DIRECTOR ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium

DR. B. L. HARTWELL
28 Rowe St., Auburndale, Mass.

DR. D. J. HISSINK
Soil Science Institute, Groningen, Holland

DR. C. B. LIPMAN
University of California, Berkeley, Calif.

DR. BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.

DR. T. L. LYON
Cornell University, Ithaca, N. Y.

DR. M. M. MCCOOL
Michigan State College, East Lansing, Mich.

DR. W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.

DR. E. A. MITSCHERLICH
University of Königsberg, Prussia

PROF. C. A. MOOERS
University of Tennessee, Knoxville, Tenn.

DR. SVEN ODÉN
Central Agricultural Experiment Station, Experimentalfaltet, Sweden

DR. THEO. REMY
Institut für Boden- und Pflanzenbaulehre, Bonn a. Rh.

PROF. G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy

DR. E. J. RUSSELL
Rothamsted Experimental Station, Harpenden, England

DR. O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.

DR. ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary

DR. J. STOKLASA
Technical High School, Prague, Czechoslovakia

PROF. CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio

PROF. N. M. TULAIKOV
Agricultural Experiment Station, Saratov, U. S. S. R.

DR. F. WEIS
Royal Agricultural and Veterinary College, Copenhagen, Denmark

PROF. S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.
Copyright, 1922, The Williams & Wilkins Company

A NEW TYPE OF HYDROMETER FOR THE MECHANICAL ANALYSIS OF SOILS

AMAR NATH PURI[1]

Irrigation Research Laboratory, Lahore, India

Received for publication October 29, 1931

Bouyoucos, in a series of papers (1, 2, 3), has discussed the development of his hydrometer method for the mechanical analysis of soils Apart from the serious criticism to which the method has been subjected by Keen (6), Bouyoucos' own comparison of the results obtained by his method and those by the standard mechanical analysis method, do not show a good agreement (2). Out of the 30 soils examined, only 16 showed a fair agreement in the percentages of silt and clay or colloids. The serious discrepancy in the rest of the soils has been explained by supposing that the standard mechanical analysis method classes fine silt along with coarse silt, and the hydrometer method with the clay. All the same the disagreement is there, and no amount of agrument as to the utility (from the practical point of view) of including fine silt in clay, can alter the fact that the hydrometer method, in its present form, cannot give the mechanical analysis of soils as we know it. It might give a set of values which might prove useful in characterizing the behavior of soils in the field, but, as such, it must be considered as an empirical method for determining one of the many "single value" constants of a soil, and should not be confused with the mechanical analysis, which carries with it a definite physical meaning: i.e., a set of values giving percentages of particles of certain well-defined sizes or settling velocities, and all methods for its determination must give essentially the same results.

The hydrometer method possesses an attractive simplicity, but it lacks the precision of theory and experiment associated with the science of pure physics. The insistance of the author on adhering to a set of arbitrarily fixed conditions, shows by itself that the method possesses no fundamental basis. Nor has its value, even as an empirical method been proved beyond dispute, because it has not been shown to give results comparable with that of any other standard method of mechanical analysis, and unless we are prepared to discard all the mass of data already collected, and accept a new and arbitrary basis for the grouping of soil particles (not according to size), the hydrometer method, as it

[1] This work was carried out by the help of a grant from the Imperial Council of Agricultural Research, and the writer takes this opportunity of recording his indebtedness to the Council. Acknowledgments are also due to the Department of Agriculture, Punjab, for the loan of apparatus and other facilities for work.

stands, will not commend itself to the majority of soil scientists. In the modified form discussed in this paper, an attempt has been made to produce an instrument of precision, which might possess all the advantages of simplicity, accuracy, and reproducibility, and at the same time should have some funda-

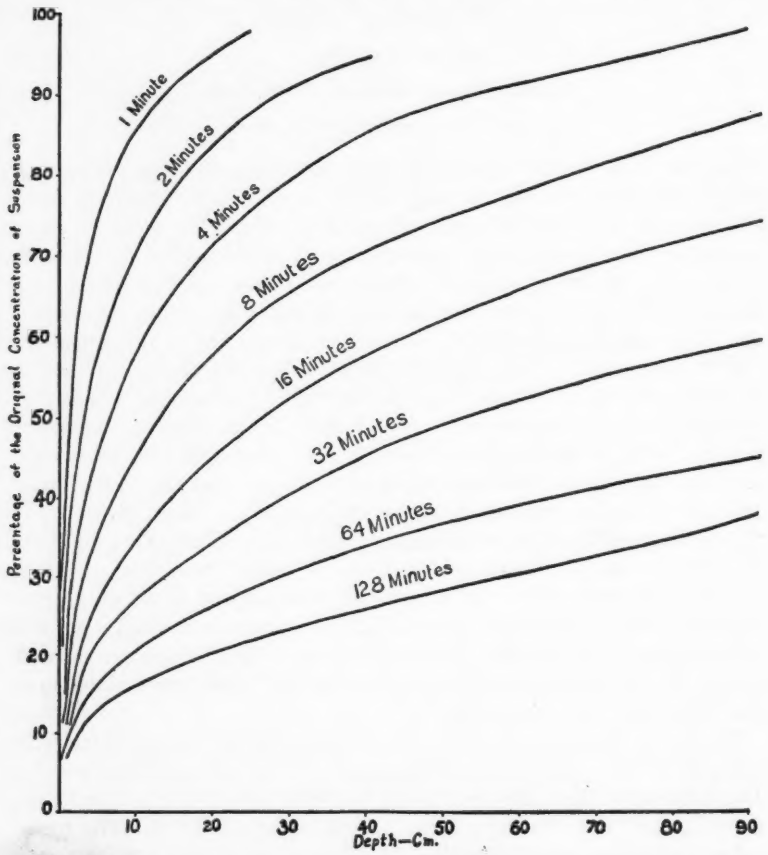


FIG. 1. CURVES SHOWING DENSITY GRADIENT IN A SEDIMENTING COLUMN AT DIFFERENT INTERVALS OF TIME

mental basis for its working, so that the necessity of working with a particular instrument, with rigidly defined specifications, is obviated.

The successful working of the hydrometer described here, depends upon the fact that the gradient of increasing density, in the suspension of a sedimenting column, becomes less and less steep as we go from top to bottom. In other words, the average density of a column of suspension, the length of which is

small compared with the total depth of the sedimenting column, may be taken without serious error as the density of its middle point. This is illustrated in figure 1, in which the density of suspension in a settling column (from top to bottom) at different intervals of time from the beginning of sedimentation, is

FIG. 2. DIAGRAM OF THE NEW TYPE OF HYDROMETER AND READING DEVICE

plotted against depth. The density in every case is expressed as percentage of the original density at the beginning of sedimentation, or the ordinates may be supposed to be the percentages of particles in suspension, the original concentration being taken as 100. The curves refer to soil P.C. 1 (table 1), and have been calculated from the summation curve obtained by the pipette method. It will be seen that there is a rapid decrease in density for the first

20–30 cm., after which the change is comparatively small. The main defect in Bouyoucos' hydrometer is that it records density changes in a region of steep density gradient, and from the nature of the curves in figure 1, the magnitude of error can be comprehended easily.

The new hydrometer shown in figure 2, consists of a wide, but short, bulb (8–10 cm. long) and a thin, long stem (about 0.4 cm. in diameter, and 60–70 cm. long). It therefore, records density changes in a column 8–10 cm. long, and situated at a distance of 50–60 cm. from the top. The settling depth is counted from the top of the sedimenting column to the mean position of the middle point of the hydrometer bulb. Another modification in the hydrometer technique is the arrangement for taking readings. The ordinary method of inserting a paper scale in the stem, is not very accurate, and an error of a few millimeters in the readings might be easily made, as a result of the water surface not providing a sharp line of reference. In this case the tip of an ordinary pin attached to a thin brass cap fitting on the top of the hydrometer stem, forms the reference point, and the readings are taken against the graduations on a burette tube, held in a special clamp. The mouth of the burette tube is closed with a brass cap having a hole in the middle through which the hydrometer stem is passed. The edges of the hole are sharpened to prevent friction that might hinder the free movement of the hydrometer. All that is necessary is to tap the burette tube gently before taking a reading. This brass cap has also a pin attached to it which is required for fixing the position of the burette tube with respect to the water surface. The tube is gradually lowered till the pin point just makes contact with the water surface. The burette tube is held in brass clamps, which keep it in position, at the same time allowing it to be pushed up or down. The brass clamps are fixed to an iron rod attached to an iron cap that can cover the top of the sedimenting cylinder, and has a hole in the middle to allow the free movement of the burette tube. This simple device enables one to take hydrometer readings within a fraction of a millimeter, and does away with the necessity of having a paper scale inside the stem. To avoid parallax the graduations on the burette tube should be all round the circumference as in the Charlottenburg type.

Since the excess of density of the suspension over that of water is proportional to the concentration, direct determinations of the variations with time of the density of the suspension at the mean resting point of the hydrometer would provide data similar in type to those obtained in the pipette method of mechanical analysis and if the foregoing assumption is reasonably correct, the two methods should give closely agreeing values.

EXPERIMENTAL

The most important point to be considered in any method of mechanical analysis is the preliminary treatment to which the soil must be subjected to bring about the maximum dispersion, for anything short of that would be arbitrary and unsatisfactory. Mere shaking, rubbing, or boiling has been

proved ineffective; on the other hand, treatment with dilute HCl and H_2O_2 (International method) is too drastic. As the result of a study of factors influencing the dispersion of soil colloids in water (8), the writer has been able to enunciate two broad generalizations:

1. All soils containing only Na as the exchangeable ion (colloids as Na saloid) in the absence of flocculating agents, are completely dispersed on coming in contact with water. They are completely reversible and can be dried and brought into suspension as many times as one likes without any shaking. They show the property of "auto-disintegration," i.e. they would go into suspension as a lump of sugar or salt would go into solution.

2. The foregoing condition is not satisfied until the neutralization of the acidoid is carried to pH 8.5.

These two principles form the basis of the (NaCl-NaOH) method developed by the author and discussed elsewhere (7). For fuller details and discussion of results the original paper should be consulted. The following outline, however, contains all the essential features:

Ten to twenty grams of soil are left in contact with 100–200 cc. of *N* NaCl for about an hour with occasional stirring. The suspension is then filtered and washed with about 500 cc. of the same solution on the filter paper. It is finally washed with a few cubic centimeter of 0.1 *N* NaCl solution, and when all of it has been drained off the remaining quantity is displaced with 10–20 cc. of water, and 0.1 *N* NaOH is gradually run in till it is alkaline to phenolphthalein (used as an external indicator, or by putting a drop of the indicator directly on the suspension). The suspension is then mechanically shaken for one hour or left for five to six hours with occasional shaking. Mechanical shaking or rubbing with a rubber pestle seems to be essential for certain red soils. For all other soils it could be dispensed with.

It is not necessary to use pure NaCl for replacement: sodium chloride containing not more than 1 per cent of calcium or magnesium salts is equally effective and can be easily prepared from ordinary common salt by adding Na_2CO_3, when the bulk of calcium and megnesium salts are precipitated. Finally the excess of Na_2CO_3 is just neutralized by adding dilute HCl. The details of the method can be varied to suit individual taste; what is required is to replace all or at least a greater part of the exchangeable ions by sodium in the clay complex.

The method of dispersion outlined was used for comparing the hydrometer and the pipette method, 2 per cent suspension being used in every case. Thirteen soils were used for the purpose. These were selected out of 48 samples with the object of having those soils which showed the greatest difference in their mechanical composition. The comparison, therefore, is even more rigid than would appear from the actual number of samples used. Two hydrometers were used, which will be referred to as No. I and No. II The bulb of the former was 9 cm. long and had a volume of 55 cc.; the latter had a bulb 6 cm. long and a volume of 74 cc. Both had a mean resting position 50 cm. below the surface.

The results given in table 1 show a very good agreement between the pipette and the hydrometer method. There is some discrepancy in the case of very coarse fractions in certain soils, but the reliability of the pipette method for particles of a limiting diameter above 0.04 mm. is questionable, for the time

TABLE 1

Mechanical analyses of soils by the hydrometer as well as the pipette method*

SOIL	METHOD	SUMMATION PERCENTAGES OF PARTICLES OF DIAMETER								
		0.002 mm.	0.004 mm.	0.006 mm.	0.008 mm.	0.01 mm.	0.02 mm.	0.04 mm.	0.06 mm.	0.08 mm.
P.C. 1	Pipette	11.3	16.0	23.6	29.0	34.6	58.1	86.3	97.6	97.4
	Hydrometer I	11.7	17.1	23.8	29.7	35.1	56.7	83.0	94.5	95.4
P.C. 2	Pipette	....	62.2	65.1	67.8	70.2	78.4	86.5	89.6	89.7
	Hydrometer I	....	62.0	67.5	70.8	73.4	81.7	86.8	88.0	89.7
P.C. 7	Pipette	....	26.6	31.4	35.3	38.6	54.2	71.4	83.6	....
	Hydrometer I	....	26.8	33.1	37.0	40.8	53.1	68.9	79.5	....
P.C. 10	Pipette	....	51.1	53.4	55.3	56.4	61.6	70.2	78.6	....
	Hydrometer I	....	48.9	54.0	55.2	56.1	62.9	68.0	71.4	....
P.C. 12	Pipette	7.2	12.5	14.6	16.4	18.0	22.9	36.7	49.9	60.7
	Hydrometer I	8.1	11.0	14.4	14.4	15.7	21.7	31.4	38.2	50.1
P.C. 19	Pipette	42.4	45.9	49.5	51.9	54.0	59.4	68.0	74.5	80.7
	Hydrometer I	40.8	44.6	46.3	48.4	51.0	57.8	65.0	68.0	71.8
P.C. 44	Pipette	....	9.7	11.7	13.9	15.7	27.6	54.2	73.8	86.2
	Hydrometer I	....	10.6	12.3	14.0	17.0	26.8	48.4	66.3	79.1
P.C. 20	Pipette	6.5	7.9	9.1	10.3	11.1	15.7	26.6	35.9	44.2
	Hydrometer I	8.1	8.5	10.2	11.9	12.3	18.3	26.3	31.4	40.8
P.C. 34	Pipette	11.3	18.8	25.0	29.6	35.0	54.2	74.6	81.4	85.0
	Hydrometer I	11.0	17.4	22.1	27.2	33.1	47.2	65.9	73.5	79.5
P.C. 39	Pipette	8.5	10.2	11.4	11.7	12.4	18.0	24.7	34.4	49.9
	Hydrometer I	....	10.1	10.7	12.5	12.5	16.9	22.5	28.7	45.0
	Hydrometer II	8.1	9.3	10.2	11.5	13.6	17.0	20.4	27.2	47.6
P.C. 27	Pipette	....	57.7	59.3	61.7	61.7	69.6	73.7	76.9	79.2
	Hydrometer I	....	55.0	58.8	61.6	63.2	69.8	73.7	76.4	78.6
	Hydrometer II	....	56.5	59.5	60.3	62.1	68.4	73.1	75.7	79.9
P.C. 45	Pipette	17.7	22.9	26.6	30.0	33.4	44.5	67.3	81.1	....
	Hydrometer I	....	20.7	25.3	30.3	33.4	46.1	64.5	78.4	87.6
	Hydrometer II	16.0	18.6	25.8	28.5	29.9	44.5	65.9	78.3	86.4
P.C. 29	Pipette	63.0	68.5	70.5	74.7	76.2	84.3	90.4	90.5	90.7
	Hydrometer I	....	64.9	71.5	74.8	77.5	85.8	91.8	92.4	92.4
	Hydrometer II	60.8	66.3	70.6	74.0	76.5	84.2	89.3	91.8	93.5

* All values refer to air-dry soil samples.

taken up in actually pipetting out a sample is large as compared to the settling velocity of the particles and it is much more likely that the hydrometer might give more reliable values in the case of such fractions. It must be admitted, however, that some disturbance in the settling particles due to the presence of the hydrometer is inevitable (4), and the low values obtained in certain cases may be partly due to that. Some error is also possible on account of the settling of the particles on the hydrometer itself tending to make it sink lower; but curiously enough the disturbance due to this cause is very little if the (NaCl-NaOH) pretreatment is used for dispersion; somehow the particles are rendered more slippery and less likely to lodge on the hydrometer. Soils merely shaken with water showed greater disturbance due to this cause.

The making and filling of the hydrometer is not difficult and a person possessing moderate skill in glass blowing can complete one in about three hours. The calibration is done by the help of a soil of known mechanical composition; a 2 per cent suspension of such a soil can be kept for this purpose.

Since the reading of the hydrometer in water must vary with the temperature, the sedimenting cylinder is kept in a water bath, through which water from the tap is kept flowing. This is quite sufficient to keep the temperature reasonably constant and no thermostat is necessary. The zero of the instrument, i.e. the reading in water, is taken just before starting the measurement by the help of a cylinder containing water and kept in the same tank. Or this can be ascertained once for all by taking readings with water at different temperatures and working out the change in the hydrometer reading per unit change in temperature.

The sedimentation cylinder can be made from a wide glass tube (about 6–7 cm. diameter) and closed at one end. The settling velocity corresponding to different fractions is adjusted at the working temperature by the help of the table given by Puri and Amin (9) or calculated from the nomographs given by Crowther (5). It is to be remembered that during sedimentation the hydrometer also moves downward for about 5–6 cm. in a 2 per cent suspension but no serious error is introduced if the mean position of the middle point is taken as the basis for computing settling times. Of course, if the summation percentages are plotted against settling velocities (v), then the position of the hydrometer can be ascertained at any time during sedimentation and v calculated therefrom.

Half a dozen hydrometers can be conveniently handled for routine work and should prove the quickest means of mechanical analysis, giving directly the summation percentage curves for soils; the results being directly comparable to the pipette method.

SUMMARY

A new type of hydrometer for the mechanical analysis of soils has been described. It consists of a short bulb (6–8 cm. long) and a long, thin stem (50–60 cm. long). The readings are taken with a special device accurate to the fraction of a millimeter.

The new hydrometer gives results closely agreeing with the standard pipette method and can replace the latter for routine mechanical analysis of soils effecting a great saving in time and labor.

REFERENCES

(1) Bouyoucos, G. J. 1927 The hydrometer as a new method for the mechanical analysis of soils. *Soil Sci.* 23: 343–350.

(2) Bouyoucos, G. J. 1928 Making mechanical analyses of soils in fifteen minutes. *Soil Sci.* 25: 473–480.

(3) Bouyoucos, G. J. 1928 The hydrometer for making a very detailed mechanical analysis of soils. *Soil Sci.* 26: 233–238.

(4) Coutts, J. R. H., and Crowther, E. M. 1925 A source of error in the mechanical analysis of sediments by continuous weighting. *Trans. Faraday Soc.* 21: 374–380.

(5) Crowther, E. M. 1928 Nomographs for use in mechanical analysis calculations. *Proc. First Internatl Cong. Soil Sci.* P. II, Comn. I: 399–404

(6) Keen, B. A. 1928 Some comments on the hydrometer method for studying soils. *Soil Sci.* 26: 261–263.

(7) Puri, A. N. 1929 A new method of dispersing soils for mechanical analysis. *Mem. Dept. Agr. India, Chem. Ser.* 10: 209–220.

(8) Puri, A. N. 1930 Studies in soil colloids: II. Factors influencing the dispersion of soil colloids in water. *Mem. Dept. Agr. India, Chem. Ser.* 11; 39–51.

(9) Puri, A. N., and Amin, B. M. 1928 A comparative study of the methods of preparation of the soil for mechanical analysis, with a note on the pipette method. Agr. Res. Inst. Pusa Bul. 175.

REPLACEABLE BASES IN THE SOILS OF SOUTHEASTERN MINNESOTA AND THE EFFECT OF LIME UPON THEM[1]

C. O. ROST AND JEAN M. ZETTERBERG

University of Minnesota

Received for publication October 31, 1931

This paper reports a study of the base capacity, the degree of unsaturation and the effect of different amounts of lime on it, and the relation of the degree of unsaturation to the hydrogen-ion concentration of the soils of southeastern Minnesota.

EXPERIMENTAL

Selection of methods

To determine the replaceable base the soil is either leached, or first treated with a preliminary solution and then leached, with some cation in solution until replacement ceases. Then the amounts of base removed in the leachate are determined by the usual quantitative methods. This may be, and in some cases is, checked by replacing the first base by a second and similar treatment with a different base or, in cases where ammonium chloride has been used, by the determination of the nitrogen. Gedroiz (5) first used ammonium chloride and large samples but later developed a method (6) in which he used hydrochloric acid and relatively small samples. Hissink (9) has used barium hydroxide and barium chloride to determine not only the replaceable base but also the exchange capacity. Kappen (13) has suggested hydrochloric acid to determine the base content. Lately Kelley and Brown (14), working on exchange capacity, have used barium hydroxide, ammonium chloride, and barium chloride.

Because of the conflicting evidence of different investigators in the use of the various methods it appeared desirable first to compare the results obtained by two of the methods on the same soils. The earlier methods of Gedroiz (5) were rejected as being too long and tedious since the large bulk of the leachate made accurate analysis difficult. The later method developed by him (6) was compared with a method suggested by Parker (20).

In the Parker method for exchange capacity 10 gm. of soil are treated at room temperature with 100 cc. of 0.1 *N* $Ba(OH)_2$, for a period of 16 to 18 hours. The suspension is then filtered by suction in a Gooch crucible. After all of the soil has been transferred to the crucible it is leached with 250 cc. of neutral

[1] Contribution from the division of soils and published with the approval of the director of the Minnesota Agricultural Experiment Station as paper 1051 of the Journal Series.

N NH_4Cl. The soil and crucible are then washed with ethyl alcohol until free of chlorides, the soil is transferred to a Kjeldahl flask, and the NH_4 is determined by distillation with MgO.

For the determination of the replaceable base content, 5 or 10 gm. of soil are placed in a Gooch crucible and leached with 250 cc. of neutral *N* $BaCl_2$. The leachings are titrated with 0.1 *N* Ba $(OH)_2$ to determine the amount of hydrogen replaced by the barium, phenolphthalein being used as indicator. The soil is then leached with *N* NH_4Cl until the leachings give no test for barium. Barium in the NH_4Cl leaching is determined as $BaSO_4$. Expressed in chemical equivalents, the amount of barium absorbed minus the hydrogen replaced gives the replaceable base content of the original soil. The replaceable hydrogen is considered to be the difference between the exchange capacity of the soil and the content of replaceable bases in the soil.

Gedroiz has suggested the use of 0.05 *N* HCl as a substitute for the normal ammonium chloride method. The hydrogen ion replaces the bases from the soil with little effect upon the bases not in the soil complex. The procedure is as follows: 15–50 gm. of soil are mixed with about 50–100 cc. of 0.05 *N* HCl. The soil is brought on to a filter and leached until there is a complete substitution of calcium. If the soil does not contain large amounts of alkaline earth carbonates 500 to 2,000 cc. of filtrate may be expected, depending upon the percentage of zeolitic bases in the soil. Several cubic centimeters of concentrated nitric acid are added to destroy the organic matter, the solution is evaporated to dryness, and the residue is heated for an hour at 125°C. to render the silica insoluble. The residue is treated with hydrochloric acid and filtered. An aliquot is used for the determination of Ca and Mg, and another for Na and K. It must be remembered that a solution of 0.05 *N* HCl extracts some iron and aluminum from the soil and that these must be removed before the calcium and magnesium are determined (6).

In the calculation of the replaceable bases by this method the iron and aluminum were not included, as Gedroiz points out that the hydrolytic effects from the hydrochloric acid are too great to allow a reasonable estimation of these elements, which have at best only a doubtful claim to true replaceable form. Nor have we attempted to determine the potassium and sodium, since the preliminary work upon the samples indicated that the amount in exchangeable form in these soils is insignificant.

The total hydrogen or unsaturation was determined by means of a method proposed by Dr. Richard Bradfield, as yet unpublished, in which it is assumed that an amount of base equal to the hydrogen present in the base complex can be replaced by a buffer solution of 0.01 *N* NH_4OH using *N* NH_4Cl as the diluent. It is comparatively simple and rapid and it is possible to handle a large number of samples at one time. The method in detail is as follows: 2 gm. of soil is treated with 100 cc. of the 0.01 *N* NH_4OH—*N* NH_4Cl buffer and shaken, the suspension allowed to stand over night, and then 50 cc. siphoned off. This is titrated with 0.01 *N* HCl, an alcoholic solution of methyl red

being used as indicator. The titration is carried to a point just below the violet red. The difference between the number of cubic centimeters of acid used and the original 50 cc. of base is equal to the milliequivalents of hydrogen present.

The hydrogen-ion concentration was determined electrometrically by means of a potentiometer using a hydrogen electrode. Air-dried samples, the moisture content of which is shown in table 2, were used in all determinations of replaceable base, replaceable hydrogen, and hydrogen ions.

Comparison of results by different methods

The data on three soils using the above methods for replaceable bases and base capacity are presented in table 1. It will be seen that very similar results were obtained by the different methods. The replaceable base as determined by the Parker and Gedroiz methods agreed closely. The latter provides a simpler and more rapid means of determining the replaceable bases and is as exact. The Bradfield method for the determination of hydrogen gave results slightly lower than the Parker method but ranks the soils in the same order. Because of their convenience and their rapidity the Gedroiz and Bradfield methods were used throughout the work in this study.

TABLE 1

Milliequivalents of replaceable bases in three soils as determined by different methods

SOIL	REPLACEABLE BASE BY PARKER METHOD	REPLACEABLE BASE BY GEDROIZ HCl METHOD	HYDROGEN BY PARKER METHOD	HYDROGEN BY BRADFIELD METHOD
19039	20	19.7	10	8.3
18908	16	17.4	16	13.0
19811	13	12.2	8	7.4

Soils used

The soils used in this investigation were taken from 28 fields in southeastern Minnesota upon which the University of Minnesota has conducted liming experiments. The fields were widely distributed and represented soil types in a triangular area 125 miles long and 90 miles wide at its widest part (fig. 1).

On five experimental fields, designated as E 1, E 2, E 3, E 4, and E 5, the liming experiments were detailed and included liming at rates varying from 1 to 8 tons an acre of finely ground limestone. On these, composite samples from the plots receiving 1, 2, 3, 4, and 8 tons of finely ground limestone as well as those from untreated plots were studied. The lime on all except E 5 had been applied in 1921, and on E 5, in 1920, a year earlier. The samples were collected in 1926, 5 years after the lime had been applied. The treatments were in triplicate and the samples used for analysis were composites taken from the three plots receiving the same treatment. They were taken in 6-inch sections from the surface to a depth of 3 feet.

On the 23 demonstration fields, designated by the letters O, D, and L, only one rate of liming, in most cases 4 tons, was used and only samples from the untreated portion of the fields were studied. The samples were composites from several borings and represented the first and second 6-inch sections and the second foot. The lime was applied in 1924 and the samples were taken 2 years later.

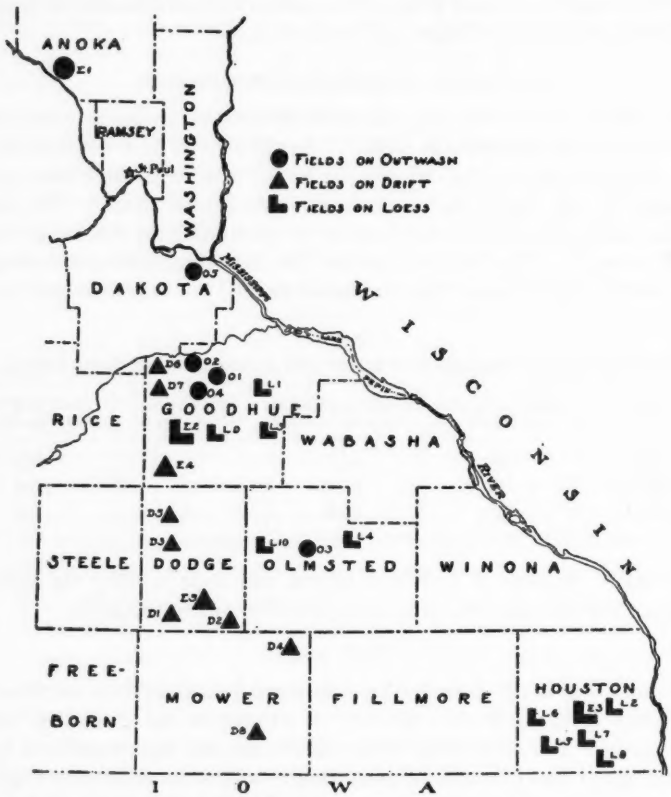


FIG. 1. MAP OF SOUTHEASTERN MINNESOTA SHOWING THE LOCATION OF THE 28 FIELDS FROM WHICH SOIL SAMPLES WERE STUDIED

The soils of the majority of the fields had been developed upon glacial drift or upon outwash left during the recession of the Iowan and Late Wisconsin glaciers. The others had been developed upon loess.

In texture the surface soils vary from loamy sand to silty clay loam (table 2). The coarsest was the Merrimac loamy sand of field E 1, with a moisture equivalent of 3.60. The texture of the subsoils also varied widely. Within the same textural class the variations were not so great. With one exception, the

texture of the 2-foot profile of each of the fields on outwash is uniform (table 2). In the case of O 4 the second foot is considerably coarser than the first foot as

TABLE 2

Texture, reaction, and moisture content of air-dry samples from three depths in the 28 fields

FIELD	TEXTURAL CLASS	MOISTURE EQUIVALENT			REACTION (pH)			MOISTURE PER CENT		
		0–6 inches	7–12 inches	13–24 inches	0–6 inches	7–12 inches	13–24 inches	0–6 inches	7–12 inches	13–24 inches
Soils developed on glacial outwash										
E 1	Loamy sand	3.6	3.9	3.0	5.7	6.3	6.4	0.53	0.55	0.50
O 1	Loamy sand	4.0	5.0	6.0	6.4	6.2	6.2	0.59	0.59	0.56
O 2	Sandy loam	13.0	18.0	15.0	5.6	6.0	6.0	1.44	1.52	1.55
O 3	Sandy loam	18.0	17.0	15.0	5.3	5.9	6.2	1.26	1.28	1.24
O 4	Sandy loam	18.0	20.0	11.0	5.6	5.8	6.0	1.55	1.6	1.12
O 5	Sandy loam	20.0	20.0	18.0	5.5	5.7	5.8	1.56	1.60	1.57
Soils developed on loess										
L 1	Silt loam	24.0	23.0	24.0	6.1	6.3	5.9	1.60	1.40	1.52
L 2	Silt loam	22.0	25.0	26.0	6.1	6.1	5.9	1.64	2.10	2.65
E 2	Silt loam	29.0	27.0	25.0	5.7	6.7	6.3	2.94	2.74	2.95
L 3	Silt loam	25.0	24.0	24.0	6.1	6.0	5.7	1.82	1.82	2.32
L 4	Silt loam	23.0	23.0	20.0	5.5	5.7	5.5	2.32	1.84	2.17
L 5	Silt loam	23.0	24.0	25.0	6.0	5.9	5.5	1.66	2.07	2.39
L 6	Silt loam	28.0	28.0	28.0	5.4	5.6	5.8	2.16	2.38	2.63
L 7	Silt loam	26.0	27.0	26.0	5.5	5.5	5.5	1.95	1.95	1.98
L 8	Silt loam	25.0	27.0	28.0	5.4	5.5	5.6	1.96	2.05	1.41
E 3	Silt loam	24.0	23.0	25.0	5.4	5.1	5.2	2.65	2.60	2.70
L 9	Silt loam	28.0	27.0	21.0	6.8	6.3	5.9	2.04	2.03	2.09
L 10	Silt loam	24.0	24.0	14.0	5.5	5.6	5.4	2.34	2.28	1.66
Soils developed on glacial drift										
D 1	Silt loam	22.0	19.0	18.0	5.6	5.7	5.6	1.99	1.06	1.85
D 2	Silty clay loam	25.0	24.0	21.0	5.5	5.3	5.2	2.48	2.22	2.17
D 3	Silty clay loam	27.0	27.0	16.0	6.0	6.0	6.1	2.06	2.06	1.75
D 4	Silty clay loam	26.0	25.0	22.0	5.4	5.5	5.6	2.58	2.18	1.97
D 5	Silty clay loam	33.0	30.0	27.0	5.4	5.6	6.6	2.94	2.77	2.75
D 6	Silty clay loam	25.0	26.0	25.0	5.9	6.1	6.2	0.69	1.63	2.25
E 4	Silty clay loam	31.0	30.0	27.0	5.3	5.8	5.8	3.40	3.34	3.03
E 5	Silty clay loam	33.0	30.0	26.0	5.4	5.3	5.5	3.40	3.40	3.16
D 7	Silty clay loam	33.0	31.0	27.0	5.6	5.8	5.9	2.52	2.50	2.28
D 8	Silty clay loam	34.0	27.0	25.0	6.8	7.0	7.5	4.13	3.53	2.75

shown by a moisture equivalent of 11 as compared to 18 and 20 for the 0–6 and 7–12 inch layers.

The soils developed on glacial drift had as a rule a subsoil somewhat lighter than the surface 6 inches (table 2). With soils developed on loess the subsoil

TABLE 3

Exchange capacity and moisture equivalent of air-dry samples from the 28 fields

DEPTH	GLACIAL OUTWASH			LOESS			GLACIAL DRIFT		
	Field	Moisture equivalent	Exchange capacity	Field	Moisture equivalent	Exchange capacity	Field	Moisture equivalent	Exchange capacity
inches			*m.e.**			*m.e.*			*m.e.*
0–6	E 1	3.6	6.4	L 1	24.0	18.7	D 1	22.0	24.9
7–12		3.9	4.8		23.0	18.4		19.0	20.9
13–24		3.0	4.3		24.0	18.3		18.0	18.6
0–6	O 1	4.0	10.9	L 2	22.0	18.8	D 2	25.0	26.0
7–12		5.0	8.6		25.0	24.1		24.0	23.3
13–24		6.0	11.7		26.0	21.0		21.0	21.2
0–6	O 2	13.0	15.9	E 2	29.0	22.5	D 3	27.0	28.7
7–12		18.0	15.5		27.0	19.5		27.0	27.2
13–24		15.0	14.7		25.0	19.4		16.0	19.7
0–6	O 3	18.0	18.5	L 3	25.0	24.5	D 4	26.0	30.8
7–12		17.0	13.9		24.0	19.5		25.0	31.4
13–24		15.0	11.9		24.0	18.9		22.0	25.0
0–6	O 4	18.0	18.5	L 4	23.0	25.2	D 5	33.0	30.9
7–12		20.0	20.5		23.0	20.0		30.0	27.5
13–24		11.0	12.0		20.0	24.2		27.0	22.8
0–6	O 5	20.0	18.9	L 5	23.0	25.6	D 6	25.0	31.2
7–12		20.0	19.0		24.0	23.6		26.0	28.9
13–24		18.0	14.0		25.0	25.7		25.0	26.5
0–6		....	....	L 6	28.0	25.8	E 4	31.0	31.5
7–12		....	....		28.0	24.0		30.0	29.2
13–24		....	....		28.0	25.6		27.0	26.6
0–6		....	....	L 7	26.0	26.8	E 5	33.0	32.4
7–12		....	....		27.0	25.2		30.0	24.3
13–24		....	....		26.0	25.6		26.0	22.3
0–6		....	....	L 8	25.0	26.9	D 7	33.0	34.0
7–12		....	....		27.0	27.4		31.0	31.9
13–24		....	....		28.0	24.3		27.0	24.4
0–6		....	....	E 3	24.0	27.7	D 8	34.0	48.0
7–12		....	....		23.0	23.9		27.0	45.1
13–24		....	....		25.0	24.5		25.0	28.5
0–6		....	....	L 9	28.0	28.9		....	....
7–12		....	....		27.0	27.1		....	....
13–24		....	....		21.0	24.5		....	....

* m.e. in this and subsequent tables indicates milliequivalents per 100 gm. soil.

TABLE 3—*Concluded*

DEPTH	GLACIAL OUTWASH			LOESS			GLACIAL DRIFT		
	Field	Moisture equivalent	Exchange capacity	Field	Moisture equivalent	Exchange capacity	Field	Moisture equivalent	Exchange capacity
inches			*m.e.**			*m.e.*			*m.e.*
0–6		....	....	L 10	24.0	31.2		....	....
7–12		....	....		24.0	26.5		....	....
13–24		....	....		14.0	16.5		....	....
0–6	Average	12.7	14.8	Average	25.0	25.2	Average	29.3	31.8
7–12		13.6	13.7		25.0	23.2		27.2	29.0
13–24		11.3	11.6		23.6	22.3		23.7	23.6

was usually as heavy as the surface soil. In a few fields, such as L 2, the subsoil had a higher moisture equivalent than the surface 6 inches, whereas on another field, L 10, the subsoil was much coarser than the surface layer.

The reaction of the soils varied from acid on fields E 4 and O 3, pH 5.3, to close to neutral on D 8, pH 6.8 (table 2). In the subsoil the variation was from a pH of 5.1 on field E 3 to a pH of 7.5 on field D 8. In general the pH rose in the lower depths. The soils on glacial drift were from calcareous parent material and in some fields, such as E 4, occasional fragments of limestone were found at the 36-inch level.

Exchange capacity

The exchange capacity, which is the total exchangeable base including hydrogen in the soil, is calculated as milliequivalents of base per hundred grams of air-dry soil. In the soils used in the study the exchange capacity varied widely. The values ranged from 6 to 48 m.e. and in general the variation can be correlated rather closely with texture of the sample (table 3). The lowest capacity of 6 m.e. was found on field E 1, which is a Merrimac loamy fine sand with a moisture equivalent of 3.6, and the largest amount, 48 m.e., was in the silty clay loam with a moisture equivalent of 34 from field D 8. This wide range and its close correlation with the texture has been found generally by workers in base exchange (14, 20).

For the measure of the colloidal material present the moisture equivalent of the sample was used. Table 3 gives the base capacity and the moisture equivalents of these soils. It is evident that the relationship is close. Especially is this true in the case of the sandy loams, as for instance fields O 3 and O 4, which have moisture equivalents of 18 and base capacities of 18 m.e. For silt loams and silty clay loams the agreement is not quite so close.

The exchange capacity of the sands was between 6 and 10.9 m.e., the lower value being for field E 1 and the higher for O 1 (table 3). The sandy loams showed exchange capacities of about 18 m.e. One, field O 2, was 15.9 m.e.

The texture was somewhat coarser than that of the other fields of the textural class as indicated by a moisture equivalent of 12.

It is more difficult to set a definite capacity for the heavier soil types since the variation is wide. In the silt loams developed on loess the fields L 1 and L 2 had an exchange capacity of 18 m.e. and L 10 had one of about 31. In general the values were about 25 m.e. In the silty clay loams on the glacial drift the variations were still greater, from 26 to 48 m.e. in 100 gm. of air-dry soil (table 3). Field D 8 having 48 is rather unusual, since the base capacity found in this group of soils averaged 32 m.e., and the majority of samples from the different fields did not vary much from this figure.

The variation in exchange capacity on individual fields as shown by samples from fields E 2 and E 4 was nearly as great as that found between fields of one textural class (table 4). On E 4 the two control plots had values of 31 and 36 m.e. in the first 6 inches and of 18.7 and 26 in the 19–24 inch depths. The values found on the surface 6 inches of E 2 were 22 and 28.6 m.e.

TABLE 4

Variations in exchange capacity on two fields

FIELD E 2			FIELD E 4		
Depth	Exchange capacity		Depth	Exchange capacity	
	Plot A	Plot B		Plot A	Plot B
inches	*m.e.*	*m.e.*	*inches*	*m.e.*	*m.e.*
0–6	28.6	22.5	0–6	36.3	31.5
7–12	19.9	19.5	7–12	31.2	29.2
13–18	21.7	21.1	13–18	28.7	27.2
19–24	20.0	17.6	19–24	18.7	26.0

The exchange capacity was lowest in the soils developed on glacial outwash and highest in the silty clay loams on drift. The soils developed on loess occupied an intermediate position. It would appear that there is a definite correlation between the exchange capacity and the texture. The numerical value of the figure representing the milliequivalents of base present was almost identical with that of the figure expressing the moisture equivalent (table 5).

Bases present

The replaceable bases compose the saturated fraction of the base complex and the hydrogen present in the base complex forms the unsaturated fraction of it. In the soils of this area, hydrogen and calcium were present in far greater quantities than the magnesium. Together, they usually constituted from 86 to 90 per cent or even more of the total exchange capacity (table 6). In general the replaceable magnesium remained fairly constant regardless of the degree of saturation or texture. On field D 8 where there was only 14.6

per cent hydrogen there was 12 per cent of magnesium while on D 4 which had 46.5 per cent hydrogen there was only 13 per cent magnesium.

The replaceable calcium in these soils is always greater than the replaceable magnesium. In general the ratio for the lighter soils was approximately 1:6 although it showed a wide variation. In the silt loams and silty clay loams the ratio remained surprisingly constant, about 1:4, falling to 1:3 or even to 1:2 when the unsaturation was very high. In milliequivalents per hundred grams of soil the magnesium was about 1.5 in the sandy loams, usually from 3 to 6 in silt loams, and slightly higher in the silty clay loams on the drift. In a few cases however it was very low, such as on fields D 2, D 5, and L 2, where it was 1.6, 1.3 and 1.6 m.e. respectively.

The amount of calcium in replaceable form is governed by the degree of unsaturation. In these unsaturated soils the quantity found in the sandy loam varied from 6 to 9.6 with an average of about 8 m.e. In heavier types the range was wider but in all cases, except field D 2 surface soil and a few

TABLE 5

Average exchange capacity and moisture equivalents of soils developed on outwash, loess, and glacial drift

DEPTH	SOILS ON OUTWASH		SOILS ON LOESS		SOILS ON DRIFT	
	Moisture equivalent	Exchange capacity	Moisture equivalent	Exchange capacity	Moisture equivalent	Exchange capacity
inches						
0–6	12.7	14.8	25.0	25.2	29.3	31.8
7–12	13.6	13.7	25.0	23.2	27.3	29.0
13–24	11.3	11.6	23.6	22.3	23.7	23.6

subsoils, the quantity of calcium was higher than that found in the best supplied sandy loams. The range in the fine textured soils was from 8.6 to 35 m.e. with an average of about 14.

The amounts of replaceable base were least in the soils developed on glacial outwash, slightly greater in the loess soils, and most in soils on the drift material. Loess soils were about 2 m.e. higher than the outwash soils in each case. Drift soils had a magnesium content equal to that found in the silt loams but the calcium was 4 or 5 m.e. greater and the hydrogen about 2.

Distribution of bases in the soil profile

Although the distribution of bases throughout the profile was somewhat variable, there was in general a decrease from the surface downward (table 6). In nearly all cases the largest amount was found in the surface layer. The decrease from the surface downward may be associated with the decrease in organic matter. In cases where there was any marked textural change this was indicated by an abrupt change in the amount of base present. Thus in field O 4 the second foot was very sandy and this was accompanied by a drop

TABLE 6

Exchange capacity and replaceable bases in soils from 28 fields

DEPTH	GLACIAL OUTWASH					LOESS					GLACIAL DRIFT				
	Field	Exchange capacity	H	Ca	Mg	Field	Exchange capacity	H	Ca	Mg	Field	Exchange capacity	H	Ca	Mg
inches		*m.e.*					*m.e.*					*m.e.*			
0–6	E 1	6.4	3.2	2.5	0.7	L 1	18.7	5.5	8.7	4.5	D 1	24.9	12.6	9.4	3.0
7–12		4.8	2.0	2.1	0.6		18.4	4.2	9.6	4.6		20.9	9.1	8.7	3.1
13–24		4.3	1.9	1.8	0.6		18.3	4.9	9.5	3.9		18.6	7.4	8.2	3.0
0–6	O 1	10.9	3.4	6.6	0.9	L 2	18.8	7.4	9.8	1.6	D 2	26.0	13.4	10.9	1.7
7–12		8.6	3.6	4.0	1.0		24.1	9.5	10.4	4.2		23.3	13.3	7.5	2.6
13–24		11.7	5.3	5.5	0.9		21.0	8.8	8.8	3.5		21.2	10.9	7.5	2.8
0–6	O 2	15.9	7.1	7.2	1.6	E 2	22.5	8.6	10.1	3.8	D 3	28.7	11.9	12.9	3.9
7–12		15.5	7.8	6.8	0.9		19.5	6.0	9.8	3.7		27.2	10.6	12.2	4.4
13–24		14.7	6.3	6.5	1.9		19.4	5.3	9.7	4.4		19.7	7.9	8.5	3.3
0–6	O 3	18.5	7.0	9.6	1.9	L 3	24.5	9.6	12.3	2.6	D 4	30.8	14.3	12.6	3.9
7–12		13.9	5.1	7.2	1.6		19.5	7.6	8.9	3.0		31.4	13.6	12.1	5.7
13–24		11.9	3.9	6.9	1.1		18.9	8.9	7.6	2.4		25.0	12.0	9.5	3.6
0–6	O 4	18.6	7.9	9.3	1.4	L 4	25.2	12.8	9.4	3.0	D 5	30.9	13.9	15.7	1.3
7–12		20.5	10.6	8.9	1.4		20.0	9.1	8.5	2.4		27.8	12.0	14.0	1.5
13–24		12.0	6.2	4.6	1.3		24.2	9.1	11.4	3.7		22.8	10.7	10.0	2.0
0–6	O 5	18.9	9.6	8.5	0.8	L 5	25.6	8.1	14.7	2.8	D 6	31.2	10.2	17.3	3.7
7–12		19.0	8.3	7.9	2.8		23.6	10.0	10.5	3.2		28.9	10.6	16.8	1.6
13–24		14.0	5.6	7.8	0.7		25.7	9.8	11.7	4.2		26.5	9.8	14.4	2.3
0–6		....	....	....	....	L 6	25.8	11.4	9.9	4.4	E 4	31.5	13.8	15.2	2.5
7–12		....	....	....	....		24.0	10.8	9.8	3.4		29.2	11.4	14.1	3.7
13–24		....	....	....	....		25.6	10.6	11.3	3.7		26.6	8.1	13.5	5.0
0–6		....	....	....	....	L 7	26.8	12.5	10.5	3.8	E 5	32.4	12.0	15.8	4.6
7–12		....	....	....	....		25.2	11.8	9.6	3.8		24.3	9.8	10.7	3.8
13–24		....	....	....	....		25.6	12.6	9.2	3.8		22.3	8.3	10.5	3.5
0–6		....	....	....	....	L 8	26.9	12.9	9.9	4.1	D 7	24.0	12.8	16.8	4.5
7–12		....	....	....	....		27.4	11.2	11.5	4.7		31.9	13.0	14.7	4.2
13–24		....	....	....	....		24.3	11.5	10.7	2.1		24.4	9.6	10.6	4.1
0–6		....	....	....	....	E 3	27.7	13.0	10.6	4.1	D 8	48.0	7.0	35.2	5.9
7–12		....	....	....	....		23.9	12.4	8.5	4.1		45.1	5.5	24.0	5.6
13–24		....	....	....	....		24.5	11.8	8.3	4.4		28.5	2.5	21.5	4.5
0–6		....	....	....	....	L 9	28.9	6.3	18.1	4.5		....	....	....	...
7–12		....	....	....	....		27.1	8.5	14.9	3.8		....	....	....	...
13–24		....	....	....	....		24.5	7.0	12.6	4.9		....	....	....	...

TABLE 6—*Concluded*

DEPTH	GLACIAL OUTWASH					LOESS					GLACIAL DRIFT				
	Field	Exchange capacity	H	Ca	Mg	Field	Exchange capacity	H	Ca	Mg	Field	Exchange capacity	H	Ca	Mg
inches		*m.e.*					*m.e.*					*m.e.*			
0–6		....	....	....	....	L 10	31.2	12.6	14.9	3.7		....	....	....	...
7–12		....	....	....	....		26.5	10.1	13.2	3.2		....	....	....	...
13–24		....	....	....	....		16.5	5.6	7.9	3.0		....	....	....	...
0–6	Aver-	....	7.9	8.6	1.4	Aver-	....	10.1	11.6	3.6	Aver-	....	12.2	16.2	3.5
7–12	age	....	7.9	7.7	1.7	age	....	9.3	10.4	3.7	age	....	10.9	14.5	3.6
13–24		....	5.5	6.4	1.2		....	8.8	9.9	3.9		....	8.7	11.4	3.4

from 20.5 m.e. in the second 6 inches to 12.0 in the second foot. Likewise on field L 10 there was a change in texture at the end of the first foot as indicated by a lowering of the moisture equivalent from 24 to 14 and a drop in the amount of base from 26.5 to 16.5 m.e. In only one field was the surface 6 inches much lower in base content than the second 6 inches and that was in field L 2 where the surface was 18.8 and the second 6 inches 24.1 m.e.

Though the decrease downward was general there was usually less drop in base content in the lower depths of silt loams developed on loess than in those soils developed on glacial outwash and drift (table 6). In all profiles the average shows but a slight decrease in the second 6 inches and on the glacial drift soils a very marked drop in the second foot.

Degree of unsaturation

Hydrogen is the most powerful of all bases as a replacing cation and once it has entered the base complex only relatively great changes in the concentration of the soil solution will change the equilibrium in respect to it. In this form hydrogen comprises one of the more important types of soil acidity. Gedroiz (6) believes that much acidity is due to the hydrogen from base complex being released to react with aluminum and iron compounds. Kappen (12) on the other hand divides acidity into four groups: hydrolytic, actual acidity due to humus, and exchangeable acidity of the base complex. Nevertheless, just how much the acidity of a soil as expressed by the hydrogen-ion concentration is affected by this type of hydrogen is doubtful. Pierre (23) has shown that with certain acid-sensitive crops the growth is more closely correlated with the unsaturation than with the acidity of the soil indicated by the pH values.

The unsaturation, expressed as percentage of hydrogen in the total base, in samples used in this study is high. For the surface 6 inches the average was 40.3 per cent and equally great for the second 6 inches and second foot. It ranged from a maximum of 57 per cent on field D 2 to a minimum of 8.6

TABLE 7

Percentage unsaturation and reaction of soils from 28 fields

DEPTH	GLACIAL OUTWASH			LOESS			GLACIAL DRIFT		
	Field	Unsaturation	pH	Field	Unsaturation	pH	Field	Unsaturation	pH
inches		*per cent H*			*per cent H*			*per cent H*	
0–6	E 1	50.9	5.7	L 1	29.5	6.1	D 1	50.5	5.6
7–12		42.1	6.3		22.9	6.3		43.5	5.7
13–24		35.0	6.4		26.9	5.9		39.7	5.6
0–6	O 1	31.2	6.4	L 2	39.4	6.1	D 2	51.5	5.5
7–12		41.7	6.2		39.5	6.1		57.0	5.3
13–24		45.3	6.2		41.8	5.9		51.5	5.2
0–6	O 2	44.6	5.6	E 2	38.3	5.7	D 3	41.6	6.0
7–12		50.4	6.0		30.2	6.7		39.0	6.0
13–24		42.9	6.0		24.8	6.3		40.1	6.1
0–6	O 3	37.9	5.3	L 3	39.1	6.1	D 4	46.5	5.4
7–12		36.7	5.9		39.2	6.0		43.4	5.5
13–24		32.8	6.2		47.0	5.7		47.9	5.6
0–6	O 4	42.5	5.6	L 4	50.9	5.5	D 5	45.0	5.4
7–12		50.0	5.8		45.5	5.7		43.6	5.6
13–24		51.4	6.0		37.7	5.5		47.0	6.0
0–6	O 5	51.7	5.5	L 5	31.7	6.0	D 6	32.7	5.9
7–12		43.7	5.7		42.3	5.9		36.6	6.1
13–24		39.8	5.8		38.2	5.5		37.1	6.2
0–6		....	...	L 6	44.3	5.4	E 4	43.8	5.3
7–12		....	...		45.0	5.6		39.1	5.8
13–24		....	...		41.4	5.8		30.3	5.8
0–6		....	...	L 7	46.6	5.5	E 5	37.0	5.4
7–12		....	...		46.9	5.5		40.2	5.3
13–24		....	...		49.3	5.5		36.8	5.5
0–6		....	...	L 8	48.0	5.4	D 7	37.6	5.6
7–12		....	...		40.9	5.5		40.8	5.8
13–24		....	...		47.3	5.6		39.5	5.9
0–6		....	...	E 3	46.8	5.4	D 8	14.6	6.8
7–12		....	...		49.5	5.1		12.2	7.0
13–24		....	...		45.8	5.2		8.6	7.5
0–6		....	...	L 9	21.8	6.8		....	...
7–12		....	...		31.3	6.3		....	...
13–24		....	...		28.6	5.9		....	...

TABLE 7—*Concluded*

DEPTH	GLACIAL OUTWASH			LOESS			GLACIAL DRIFT		
	Field	Unsaturation	pH	Field	Unsaturation	pH	Field	Unsaturation	pH
inches		*per cent H*			*per cent H*			*per cent H*	
0–6		....	...	L 10	40.4	5.5		....	...
7–12		....	...		37.9	5.6		....	...
13–24		....	...		34.1	5.4		....	...
0–6	Average	43.1		Average	39.7	...	Average	40.1	...
7–12		44.1			39.3	...		39.6	...
13–24		41.2			38.6	...		37.9	...

per cent on D 8 (table 7). The variation seems to be independent of the texture, as the average unsaturation is approximately equal on all textural groups.

The unsaturation in the upper 2 feet of the profile is exceedingly variable and the variation could not be correlated with either the texture or the organic matter. In those fields for which determinations were made on the third foot the percentage unsaturation in the last foot is regularly less than that in the upper 2 feet (table 8). On the heavier soils and especially on field E 4, in which the calcerous subsoil is encountered shortly below the 36-inch depth, is the decrease very marked. On the loamy sand of field E 1 this drop is less, as though excessive leaching had caused the removal of saturating cations to greater depths in the coarser soil.

Relation of unsaturation to pH

The pH as a measure of the active acidity represents the hydrogen-ion concentration in the soil solution. One would expect from the nature of the exchange complex a certain interrelation between the pH, which represents the hydrogen in the soil solution, and the degree of unsaturation, which represents the hydrogen in exchangeable form. The hydrogen in the latter case is probably potential hydrogen and as such is a source for the active hydrogen removed from the soil. There are, however, so many factors which influence the pH of a soil besides the hydrogen of the exchange complex that a close relationship is not always discernible in a consideration of only the pH and the degree of unsaturation.

In the soils used in this investigation a general relationship is found between the pH and the degree of unsaturation. That is, usually with a greater degree of unsaturation there is a corresponding lower pH. That this does not always hold may be seen from table 9. As has been mentioned, texture appears to have no effect upon the degree of unsaturation or the pH or upon the correlation of these.

Between the pH values 5.8 and 6.2 there are greater variations than either above or below this range. It is quite possible that this increased variation

TABLE 8

Percentage unsaturation on experimental fields

DEPTH	FIELD E 1	FIELD E 2	FIELD E 3	FIELD E 4	FIELD E 5
inches					
0–6	50.9	38.3	46.8	43.8	37.0
7–12	42.1	30.2	49.5	39.1	40.2
13–18	27.7	33.2	50.6	30.2	41.1
19–24	42.3	19.4	40.9	30.4	32.4
25–30	47.7	24.2	39.7	30.8	30.8
31–36	42.9	26.1	37.1	19.5	32.6

TABLE 9

Percentage unsaturation and reaction in first and second 6 inches and second foot, arranged according to increasing pH

0–6 INCHES			7–12 INCHES			13–24 INCHES		
Field	pH	Unsaturation	Field	pH	Unsaturation	Field	pH	Unsaturation
		per cent H			*per cent H*			*per cent H*
E 4	5.3	43.8	E 3	5.1	49.5	E 3	5.2	46.0
O 3	5.3	37.9	E 5	5.3	40.2	D 2	5.2	51.5
E 5	5.4	37.0	D 2	5.3	57.0	L 10	5.4	34.1
E 3	5.4	46.8	D 4	5.5	43.4	E 5	5.5	37.0
L 8	5.4	48.0	L 7	5.5	46.9	L 4	5.5	37.7
L 6	5.4	49.3	L 8	5.5	40.9	L 7	5.5	49.3
D 4	5.4	46.5	L 6	5.6	45.0	L 5	5.5	38.2
D 5	5.4	45.0	L 10	5.6	37.9	D 1	5.6	39.7
D 2	5.5	51.5	D 5	5.6	43.6	D 4	5.6	47.9
O 5	5.5	51.7	D 1	5.7	43.5	L 8	5.6	47.3
L 4	5.5	50.9	L 4	5.7	45.5	L 3	5.7	47.0
L 7	5.5	46.6	O 5	5.7	43.7	E 4	5.8	30.3
L 10	5.5	40.4	E 4	5.8	39.1	L 6	5.8	41.4
O 2	5.6	44.6	O 4	5.8	50.0	O 5	5.8	39.8
O 4	5.6	42.5	D 7	5.8	40.8	D 7	5.9	39.5
D 7	5.6	37.6	O 3	5.9	36.7	L 2	5.9	41.8
D 1	5.6	50.5	L 5	5.9	42.3	L 1	5.9	26.9
E 2	5.7	38.3	L 3	6.0	39.2	L 9	5.9	28.6
E 1	5.7	50.9	O 2	6.0	50.4	O 2	6.0	42.9
D 6	5.9	32.7	D 3	6.0	39.0	O 4	6.0	51.4
L 5	6.0	31.7	D 6	6.1	36.6	D 5	6.0	47.0
D 3	6.0	41.6	L 2	6.1	39.5	D 3	6.1	40.1
L 3	6.1	39.1	O 1	6.2	41.7	O 3	6.2	32.8
L 2	6.1	39.4	L 9	6.3	31.3	O 1	6.2	45.3
L 1	6.1	29.5	L 1	6.3	22.9	D 6	6.2	37.1
O 1	6.4	31.2	E 1	6.3	42.1	E 2	6.3	26.0
D 8	6.8	14.6	E 2	6.7	30.2	E 1	6.4	36.0
L 9	6.8	21.8	D 8	7.0	12.2	D 8	6.5	8.6

may be due to a considerable extent to the fact that this is the borderline between distinctly acid soils and those which are neutral. In this range the degree of unsaturation goes to as high as 51.4 per cent, a value equal to any except that of field D 2, and as low as 29.6 per cent, which is no greater than that found in one sample from field E 2 with a pH of 6.7.

Near the neutral point the unsaturation was rather uniformly low, usually below 30 per cent, a limit which has been generally found by other workers. This would seem to indicate that the basic reacting substances in the soil are able to neutralize the acidity of the soil as measured by the hydrogen-ion concentration before they completely saturate the base complex. That is to say that even though the pH is 7.0 or above there may still be hydrogen present in exchangeable form which is difficultly replaceable and is not replaced before a pH of approximately 8.5 is reached (13).

In the more acid soils the degree of unsaturation was almost invariably high. In all cases it was greater than 30 per cent and frequently as high as 50 per cent. With five exceptions, L 1, L 9, L 10, D 6, and E 4, all of the samples which had a pH below 6.0 had an unsaturation above 35 per cent. Of those below a pH of 5.5 the great majority were above 44 per cent unsaturated.

Harada (7) has reported a close agreement between the pH and the degree of unsaturation. Other investigators (11), however, have observed the same general relationship reported in the foregoing. Wilson (30) working with soils of New York found a correlation between the exchangeable calcium and the hydrogen-ion concentration. With the soils used in this study the relationship between exchangeable lime and pH is less marked than between the pH and the degree of unsaturation. Our data would indicate that the bases in the exchange complex in a soil do not change as rapidly as the pH and that soils of the same pH value may have widely different degrees of unsaturation.

Effect of lime on the exchange complex

A comparison of the soils from the limed plots with those from the untreated plots on the same field brings forth some interesting data concerning the effect of lime. The samples for this study were taken on the five experimental fields from plots receiving 1, 2, 3, 4, and 8 tons an acre of finely ground limestone as well as from untreated or control plots. The lime had been applied in 1920 or 1921, alfalfa seeded in the spring of 1922, and the fields kept continuously in alfalfa until after the samples were taken in the autumn of 1926. On fields E 1, E 2, E 3, and E 4 finely ground limestone, all of which passed through a 100-mesh sieve, was applied. Hydrated lime was applied on field E 5. The composition of the liming material is presented in table 10. With all the fields except E 5 two sets of untreated plots have been used as controls throughout the study.

Rost and Fieger (25) calculated that the hydrated lime was equal in effectiveness to twice the amount of finely ground limestone. When the CaO equivalent for the MgO is calculated the content of the CaO for the two forms

is: finely ground limestone, 41.95 per cent, and hydrated lime, 88.30 per cent.

The soils of these fields varied in texture from a loamy sand on field E 1 to a silty clay loam on field E 5 (table 11). The reaction of the surface soil of the fields as expressed by the hydrogen-ion concentration was acid and ranged from pH 5.7 to 5.3 (table 11). On fields E 1, E 2, and E 4 it decreased below

TABLE 10

Chemical composition of liming materials used

MATERIAL	INSOLUBLE IN HCl	CaO	MgO
	per cent	*per cent*	*per cent*
Finely ground limestone	22.21	30.14	8.71
Hydrated lime	0.06	47.11	29.66

TABLE 11

Moisture equivalent and reaction of samples from untreated plots of the experimental fields

DEPTH	FIELD E 1		FIELD E 2		FIELD E 3		FIELD E 4		FIELD E 5	
	Moisture equivalent	pH	Moisture equivalent	pH	Moisture equivalent	pH	Moisture equivalent	pH	Moisture equivalent	pH
inches										
0–6	3.6	5.7	29.2	5.7	23.6	5.4	30.7	5.3	32.8	5.4
7–12	3.9	6.3	26.9	6.7	22.5	5.2	29.6	5.8	29.5	5.3
13–18	3.0	6.4	25.1	6.3	24.7	5.1	26.9	5.7	26.1	5.4
19–24	3.0	6.1	25.0	6.4	24.8	5.5	26.8	6.1	26.0	5.8
25–30	2.7	6.4	23.9	6.4	25.6	...	22.2	7.0	20.1	5.8
31–36	2.7	7.3	23.6	6.9	25.5	5.3	22.0	6.6	20.0	6.1

TABLE 12

Percentage of organic matter ($N \times 20$) in representative profiles of the experimental fields

DEPTH	FIELD E 1	FIELD E 2	FIELD E 3	FIELD E 4	FIELD E 5
inches					
0–6	1.0	5.4	3.8	6.2	7.6
7–12	0.6	4.0	2.0	4.4	4.8
13–24	0.2	2.2	1.0	2.0	2.2
25–36	0.2	1.0	0.6	1.0	0.8

the surface 6 inches and on field E 4 below the 18-inch level. In field E 3 the reaction was much the same throughout the profile. In organic matter the silty clay loams on E 4 and E 5 were best supplied. Fields E 2 and E 3 carried somewhat lower amounts and E 1 the least, having only 1.0 per cent in the surface section (table 12).

The exchange capacity of the untreated plots varied rather widely, as is

TABLE 13

Exchange capacity in milliequivalents per 100 gm. of air-dry soil from plots on experimental fields

DEPTH	LIME 8 TONS	LIME 4 TONS	LIME 3 TONS	LIME 2 TONS	LIME 1 TON	Untreated	
inches						Set A	Set B
			Field E 1				
0–6	11.25	8.77	5.94	8.57	7.65	6.41	7.85
7–12	7.78	6.13	7.29	5.27	4.71	4.77	6.64
13–18	6.10	7.86	6.63	4.67	4.93	4.52	5.30
19–24	5.69	6.10	3.85	6.47	3.90	4.06	5.19
25–30	6.35	.....	.....	3.98	.....	.....	5.03
31–36	4.14	.....	.....	5.57	.....	....	6.52
			Field E 2				
0–6	34.5	30.1	29.2	31.9	26.0	28.6	22.5
7–12	15.6	24.6	25.5	23.2	24.9	19.9	19.5
13–18	20.8	17.5	24.2	19.1	22.4	21.7	21.1
19–24	16.1	23.0	23.1	24.0	22.9	20.0	17.6
25–30	13.6	26.4	26.6	24.7	21.0	24.7	16.6
31–36	17.5	17.7	23.5	19.7	22.9	18.8	20.7
			Field E 3				
0–6	36.86	27.22	25.71	25.78	27.63	27.42	27.74
7–12	22.86	25.44	24.68	20.84	22.75	23.87	25.04
13–18	24.20	22.79	22.67	20.46	20.51	23.57	27.07
19–24	24.30	21.72	22.11	21.13	20.92	24.31	22.00
25–30	25.81	23.81	24.30	22.52	24.59	23.91	22.39
31–36	22.69	24.27	30.37	22.79	27.17	25.49	22.09
			Field E 4				
0–6	33.9	34.8	32.9	33.9	33.0	36.3	31.5
7–12	28.0	32.0	32.5	28.5	28.0	31.2	29.2
13–18	26.2	27.3	29.4	27.0	25.6	28.7	27.2
19–24	20.9	24.6	22.4	27.2	26.7	18.7	26.0
25–30	19.6	22.4	20.4	21.9	23.4	17.2	21.8
31–36	19.6	21.8	22.0	20.1	22.2	17.0	18.5
			Field E 5				
0–6	35.29	31.7	.....	33.48	.....	32.43	.....
7–12	24.23	25.30	.....	22.75	.....	24.33	.....
13–18	26.05	26.47	.....	24.87	.....	24.32	.....
19–24	20.53	20.99	.....	20.4	.....	20.33	.....
25–30	15.72	15.80	.....	18.88	.....	19.42	.....
31–36	17.41	20.63	.....	17.77	.....	19.58	.....

shown in table 13. The loamy sand of field E 1 had a base capacity of 6.8 m.e., and the silty clay loams of E 4 and E 5, both developed on glacial drift, of 31 and 36 m.e. on two sets of plots on the former and of 32 m.e. on the latter. Field E 3, a silt loam, had an exchange capacity of 27 m.e., whereas for E 2, also a silt loam, it was 28 on one set of control plots and 22 on the other. The soil of the last two fields have been developed on loess.

The 8-ton application of lime produced on all fields but E 4 an increase in the total base capacity of the soil (table 13). On that field the increase of 2 m.e. over the lower control is still less than the exchange capacity of 36.3 on the higher control. The increase in exchange capacity caused by 8 tons of lime on field E 2 was 6 m.e. over the higher control plot and of 12 over the lower one. On E 3 an increase of 9 m.e. is shown. Upon both E 1 and E 5 a rise of about 3 or 4 m.e. can be observed, although relatively this amount represents a considerably greater change on E 1 than it does on E 5, which has a greater initial capacity. Only upon field E 2 did any increase in exchange capacity appear to be caused by an application of less than 8 tons of lime. Here the 4-, 3-, and 2-ton applications gave exchange capacities greater than that of the low control sample though not much greater than that of the high one. These data confirm the findings of other investigators (26) that the addition of basic substances tends to increase the exchange capacity of the soil.

Effect of lime on replaceable calcium and magnesium

The calcium and magnesium content on the more heavily limed plots was in most cases several millequivalents higher than that in the untreated soils (tables 14 and 15). With the 8-ton application the calcium and magnesium content was 5 m.e. more than on the untreated plot on field E 1, 14 more on E 2, 11 more on E 3, and 9 more on E 5. On E 4 there was no apparent increase in the calcium and magnesium on the plots to which 8 tons of lime had been applied over that in the higher control plot. When calculated as per cent of total base, however, the data show an increase of 6 per cent over the higher check and of 10 per cent over the lower one. On the other fields the increase ranges in percentage from 50 on field E 1 to 20 or 30 on E 2, E 5, and E 3. The amount of increase seems to be more or less governed by the base capacity of the soil, the soils with lower exchange capacities becoming more nearly saturated with calcium and magnesium upon liming than do the finer textured soils with high exchange capacities.

In general the increase of calcium and magnesium in the base complex was correlated with the amount of lime applied. Thus the 8-ton application usually produced at least twice as much increase in the calcium and magnesium as did the 4-ton treatment. On field E 4, however, the 8-, 4-, and 3-ton applications produced about equal effects.

The point at which an effect from applications of lime can be observed appears dependent upon the individual soil. Usually in the soils which were

TABLE 14

Replaceable calcium in milliequivalents per 100 gm. of air-dry soils from plots on the experimental fields

DEPTH	LIME 8 TONS	LIME 4 TONS	LIME 3 TONS	LIME 2 TONS	LIME 1 TON	Untreated	
inches						Set A	Set B
				Field E 1			
0–6	8.20	4.74	3.57	5.28	3.89	2.49	3.00
7–12	3.70	3.24	3.89	2.67	2.28	2.14	3.10
13–18	2.70	3.46	3.03	2.21	2.25	1.89	2.60
19–24	3.30	2.53	1.85	2.49	2.64	1.78	2.20
25–30	2.60	.....	.....	1.78	.....	.....	2.40
31–36	2.20	.....	.....	2.85	.....	.....	2.60
				Field E 2			
0–6	24.0	17.0	12.8	16.7	15.2	14.9	10.1
7–12	5.3	12.0	11.5	10.2	11.4	10.7	9.8
13–18	9.3	9.9	10.5	8.7	11.0	10.5	9.4
19–24	4.3	11.3	10.7	10.7	12.1	10.9	10.1
25–30	5.1	12.2	12.8	10.8	12.3	12.1	8.4
31–36	10.8	6.2	13.1	13.2	12.2	12.3	10.2
				Field E 3			
0–6	17.31	11.70	10.63	10.03	10.67	12.00	10.60
7–12	8.74	9.17	9.00	7.88	8.67	9.96	8.50
13–18	9.30	8.38	8.21	7.78	7.17	7.49	9.20
19–24	8.90	9.03	9.24	8.42	8.56	8.42	8.30
25–30	9.70	10.31	11.24	10.50	10.60	9.74	9.60
31–36	9.20	11.49	12.53	11.60	11.67	11.38	10.42
				Field E 4			
0–6	18.9	19.7	19.8	16.1	16.1	16.3	15.2
7–12	14.8	13.8	14.0	12.2	11.7	13.6	14.1
13–18	11.0	12.7	12.6	12.0	12.2	12.6	12.6
19–24	10.9	12.5	12.9	13.9	13.9	12.1	14.5
25–30	10.7	13.9	11.8	11.8	12.0	9.6	13.0
31–36	10.7	13.5	11.6	11.9	11.3	10.6	12.2
				Field E 5			
0–6	22.00	17.63	.....	19.70	.....	15.80	.....
7–12	10.20	11.31	.....	9.38	.....	10.70	.....
13–18	11.10	11.42	.....	11.78	.....	10.70	.....
19–24	9.30	11.74	.....	10.67	.....	10.40	.....
25–30	8.10	9.06	.....	10.63	.....	9.90	.....
31–36	9.20	14.45	.....	10.99	.....	9.80	.....

TABLE 15

Replaceable magnesium in milliequivalents per 100 gm. of air-dry soil from plots on experimental fields

DEPTH	LIME 8 TONS	LIME 4 TONS	LIME 3 TONS	LIME 2 TONS	LIME 1 TON	UNTREATED	
inches						Set A	Set B
			Field E 1				
0–6	3.05	0.83	0.97	2.29	1.96	0.72	0.85
7–12	1.28	1.69	0.90	1.00	0.63	0.63	0.74
13–18	0.70	1.80	0.86	0.55	0.88	0.63	0.70
19–24	0.79	1.57	1.00	0.98	0.56	0.68	0.79
25–30	0.45	....	....	1.00	....	....	0.63
31–36	0.74	....	....	0.72	....	....	1.12
			Field E 2				
0–6	7.5	6.7	3.6	6.2	2.0	2.3	3.8
7–12	3.5	6.0	4.0	4.0	4.5	1.8	3.7
13–18	4.5	2.4	4.9	3.6	3.6	3.2	4.7
19–24	3.6	5.5	5.4	6.5	3.2	2.1	4.1
25–30	5.5	7.4	6.6	5.9	4.5	5.6	4.2
31–36	3.5	7.7	6.2	2.6	6.5	1.9	5.1
			Field E 3				
0–6	10.5	5.32	4.88	4.35	4.96	4.22	4.14
7–12	3.92	4.27	3.68	2.96	2.88	3.91	4.14
13–18	4.30	3.61	3.26	3.48	3.24	2.88	4.12
19–24	5.40	4.09	5.07	3.71	4.16	5.09	4.70
25–30	5.91	5.70	5.86	4.62	5.39	5.57	3.89
31–36	7.09	5.78	10.64	5.19	7.90	6.71	3.47
			Field E 4				
0–6	3.8	3.9	3.1	5.6	5.9	5.8	2.5
7–12	2.0	5.2	6.5	5.1	5.5	4.6	3.7
13–18	4.2	4.0	5.6	5.8	5.4	4.5	6.4
19–24	3.2	4.7	2.9	7.5	6.8	3.2	3.6
25–30	5.1	4.3	3.8	6.5	7.0	5.0	2.2
31–36	3.4	7.2	5.6	6.4	5.9	4.0	2.7
			Field E 5				
0–6	7.09	4.67	....	5.18	....	4.63	....
7–12	3.43	3.79	....	4.17	....	3.83	....
13–18	4.95	4.85	....	4.09	....	3.62	....
19–24	3.63	4.35	....	3.93	....	3.33	....
25–30	3.22	3.34	....	3.95	....	3.52	....
31–36	4.01	5.48	....	3.98	....	3.38	....

used in this investigation this point appeared between the 3- and 4-ton applications. Except with field E 1 it was impossible to note any change in the exchange complex, until at least 3 tons of limestone had been applied.

Effect of lime upon unsaturation and replaceable hydrogen

As was the case with calcium and magnesium entering the base complex, no effect of the lime applied was shown by a decrease in the hydrogen content and a subsequent decrease in the unsaturation until at least 3 or 4 tons of lime had been applied. Similarly also the hydrogen decrease was more or less proportional to the amount of lime applied (tables 16 and 17).

The increase in calcium and magnesium was in most, but not all cases, coincident with a decrease in hydrogen. For instance on field E 3 the replaceable hydrogen in the first 6 inches decreased 2 m.e. although the calcium and magnesium content was scarcely affected by the 3- and 4-ton applications of limestone (tables 14, 15, and 16). On field E 1 the calcium increased about 1.5 m.e. but the hydrogen did not vary. In general the increase in basic ions was accompanied by a decrease in hydrogen. The exchange was rarely equivalent. In the majority of cases the calcium and magnesium absorbed was greater than the hydrogen replaced. This discrepancy in the exchange would substantiate the conclusion mentioned before, that basic substances increase the adsorptive capacity of a soil. According to Kelley and Brown (15) the exchange of cations should be stochiometric or approximately so.

On field E 1, 1 ton of lime decreased the unsaturation as much as 4 tons of lime, although not to an equal depth. In the case of the 1-ton application the unsaturation in the second 6 inches amounts to 38.2 per cent and with the 4-ton application for the same section it is 30.8 per cent. As the unsaturation is 41 and 42 per cent in this section of the control plots one can consider the decrease with the 4-ton application as being due to the lime and not within the limits of experimental error. Neither the 1-, 2-, nor 3-ton applications of lime had any effect below the first foot on field E 1. The 4-ton application shows a quite definite effect on the second foot (table 17).

The only plots upon which the addition of lime completely saturated the base complex were those on field E 1 which received 8 tons of lime. Here in the first 6 inches there was no replaceable hydrogen or unsaturation. Below this section, however, it is difficult to indicate the point to which the lime was effective, but certainly it was effective to the end of the first foot. The pH of the plot receiving 8 tons was 8.3, which agrees well with the work of Kappen (13), who has suggested that complete saturation does not take place below a pH of 8.5. Parker (21) has taken a pH of 7.0 as the point at which complete saturation occurs.

On the other experimental fields the unsaturation in most cases was lowered to less than 30 per cent by an application of 3 or more tons of limestone. There appears to have been no effect from lime upon the unsaturation in the base complex below the surface 6-inch layer of these fields.

TABLE 16

Replaceable hydrogen in milliequivalents per 100 gm. of air-dry soil from plots on experimental fields

DEPTH *inches*	LIME 8 TONS	LIME 4 TONS	LIME 3 TONS	LIME 2 TONS	LIME 1 TON	UNTREATED	
						Set A	Set B
				Field E 1			
0–6	0.0	3.2	1.4	1.0	1.8	3.2	4.0
7–12	2.8	1.2	2.5	1.6	1.8	2.0	2.8
13–18	2.7	2.6	2.8	2.0	1.8	2.0	2.0
19–24	1.6	2.0	1.0	3.0	0.7	1.6	2.2
25–30	3.3	....	....	1.2	....	....	2.0
31–36	1.2	....	....	2.0	....	....	2.8
				Field E 2			
0–6	3.0	6.4	8.0	9.0	8.8	11.4	8.6
7–12	6.8	6.6	10.0	9.0	9.0	7.4	6.0
13–18	7.0	5.2	8.8	6.8	7.8	8.0	7.0
19–24	8.2	6.2	7.0	6.8	7.6	7.0	3.4
25–30	3.0	6.8	7.2	8.0	4.2	7.0	4.0
31–36	3.2	3.8	4.2	3.9	4.2	4.6	5.4
				Field E 3			
0–6	9.4	10.2	10.2	11.4	12.0	11.2	13.0
7–12	10.2	12.0	12.0	10.0	11.2	10.0	12.4
13–18	10.6	10.8	11.2	9.2	10.1	13.2	13.7
19–24	10.0	8.6	7.8	9.0	8.2	10.8	9.0
25–30	10.2	7.8	7.2	7.4	8.6	8.6	8.9
31–36	6.4	7.0	7.2	6.0	7.6	7.4	8.2
				Field E 4			
0–6	11.2	11.2	10.0	12.2	11.0	14.2	13.8
7–12	11.2	13.0	12.0	11.2	10.8	13.0	11.4
13–18	11.0	10.6	11.2	9.2	8.0	11.6	8.2
19–24	6.8	7.4	6.6	5.8	6.0	3.4	7.9
25–30	3.8	4.2	4.8	3.6	4.4	2.6	6.6
31–36	5.5	1.1	4.8	1.8	5.0	2.4	3.6
				Field E 5			
0–6	6.2	9.4	....	8.6	....	12.0	....
7–12	10.6	10.2	....	9.2	....	9.8	....
13–18	10.0	10.2	....	9.0	....	10.0	....
19–24	7.6	4.9	....	5.8	....	6.6	....
25–30	4.4	3.4	....	4.3	...	6.0	....
31–36	4.2	0.7	....	2.8	....	6.4	....

TABLE 17

Effect of different amounts of lime on unsaturation of soils of the experimental fields

DEPTH	LIME 8 TONS	LIME 4 TONS	LIME 3 TONS	LIME 2 TONS	LIME 1 TON	UNTREATED	
inches						Set A	Set B
				Field E 1			
0–6	0.0	36.4	23.5	11.4	23.5	49.9	50.9
7–12	35.9	19.5	34.2	30.8	38.2	41.9	42.1
13–18	44.2	33.0	41.8	42.8	36.5	44.2	27.7
19–24	28.1	32.7	25.9	46.3	17.9	39.4	42.3
25–30	51.9	....	....	30.1	....	....	47.7
31–36	28.9	....	....	35.9	....	....	42.9
				Field E 2			
0–6	8.7	21.3	27.4	28.3	33.9	39.9	38.3
7–12	43.6	26.9	39.3	38.8	36.2	37.2	30.2
13–18	33.7	29.8	36.4	35.6	34.1	36.9	33.2
19–24	51.0	27.0	30.4	28.4	33.2	35.0	19.4
25–30	22.1	25.8	27.1	32.4	20.0	28.4	24.2
31–36	18.3	21.5	17.9	19.8	18.4	24.5	26.1
				Field E 3			
0–6	25.3	37.4	39.6	44.2	43.4	40.8	46.8
7–12	44.6	47.1	48.6	48.8	49.2	41.8	49.5
13–18	43.8	47.3	49.4	44.9	49.2	56.0	50.6
19–24	41.1	39.5	35.2	42.5	39.1	44.4	40.9
25–30	39.5	32.7	29.6	32.8	34.9	35.9	39.7
31–36	28.2	28.8	23.7	26.3	27.9	29.0	37.1
				Field E 4			
0–6	33.1	32.2	30.6	36.0	33.4	39.2	43.8
7–12	40.0	40.7	27.0	39.3	38.6	41.7	39.1
13–18	42.0	38.9	38.1	34.1	31.3	40.5	30.2
19–24	32.6	30.1	29.5	21.4	22.5	18.2	30.4
25–30	19.4	18.8	23.6	16.5	18.9	16.0	30.8
31–36	28.1	5.1	21.9	9.0	22.6	14.2	19.5
				Field E 5			
0–6	17.5	29.6	....	25.6	....	37.0	....
7–12	43.7	40.3	....	40.4	....	40.2	....
13–18	38.3	38.5	....	36.1	....	41.1	....
19–24	37.0	23.3	....	28.4	....	32.4	....
25–30	27.9	21.5	....	22.7	....	30.8	....
31–36	24.1	3.4	....	15.7	....	32.6	....

The data presented in tables 16 and 17 indicate that the effect of lime applied to the surface in sufficient amounts decreased the unsaturation of the soils. The amount of decrease varies more or less with the individual soil. Complete saturation can be expected only when the pH is above 8.3.

Penetration of lime as shown by effect upon base complex

The effect of 8 tons of lime upon the base complex was confined to the surface 6 inches on fields E 4, E 5, E 3, and E 2 and to a depth of 2 feet on field E 1. The depth to which the lime had reached was shown in two ways, first by an increase in the calcium and magnesium content, and second by a decrease in the hydrogen content and the degree of unsaturation (tables 15, 16, and 17). This effect was apparent on the surface of all plots which received heavy applications of lime. On the sand the changes extended deeper.

Previously Rost and Fieger (25) in their work on the effect of lime on the hydrogen-ion concentration of these soils had observed the penetration of lime into the lower depths as shown by the change in the hydrogen-ion concentration. They reported that the effect of an 8-ton application of limestone extended to a depth of 12 inches upon fine-textured soils and to a depth of more than 3 feet upon the sand of field E 1. The penetration of the lime in these soils as determined by the changes in the exchange complex is not so great. It is possible, however, as a study of the data on the effect of lime will show, that in many cases as much as 2 tons of lime could penetrate into the lower depths of the soil and still not affect the exchange complex noticeably. From a comparison of the data obtained by Rost and Fieger on the hydrogen-ion concentration and that obtained in this study it would appear that the lime applied at the surface of any soil except sands has but a small effect upon the exchange complex below the depth of mechanical incorporation although it may affect the hydrogen-ion concentration to greater depth.

Buffer capacity

The effectiveness of lime as a corrective of acidity is limited by the buffer capacity of the soil. This is the inherent ability of a soil to resist changes in its hydrogen-ion concentration through the application of substances which would tend to either increase or decrease the hydrogen-ion concentration. Hoagland and Christie (10) have shown that this capacity is greater in fine textured soils than in coarse and that it will require less base to cause a definite change in reaction on a sand than on a fine textured soil.

Various explanations of this phenomenon have been advanced by investigators. The data from the five experimental fields indicate that the buffer capacity may be directly connected with and even dependent upon the base capacity of the soil. It is to be expected that 8 tons of limestone, regardless of whether it is applied upon a silty clay loam soil such as field E 4 or upon a loamy sand as in field E 1, will produce a somewhat equal concentration in the soil solution. The ratio of this concentration to the unsaturation in the base capacity of a soil such as a loamy sand is much greater than it is on a fine textured soil. In the former case, if an unsaturation of 50 per cent be assumed, the lime has only to replace about 4 m.e. of hydrogen per 100 gm. of soil, since in sandy soils used in this study the exchange capacity is rarely over 8 m.e.

In the case of a silty clay loam with an exchange capacity of 34 m.e. and a 50 per cent unsaturation, the same amount of lime would have to replace at least 17 m.e. of hydrogen per 100 gm. of soil. It should then be about four times as effective on the first soil as on the second if the lime is considered equal in its effective power in both cases.

That such may be the case appears likely from a study of the effect of the 8-ton application of lime stone upon the degree of unsaturation in the five experimental fields. The sample from field E 1 had the greatest unsaturation, 50 per cent, and field E 4 had only 43 per cent. On other fields the unsaturation was less than 50 per cent. Despite the fact that field E 4 has less unsaturation than field E 1, the unsaturation is reduced only to 33.1 per cent. This field with the highest base capacity has been the least corrected in unsaturation by an 8-ton application of ground limestone. On field E 5 with the next highest base capacity, 32 m.e., the unsaturation was reduced slightly more, or from 37 per cent to 30 per cent. This decrease is on the plot which

TABLE 18

Unsaturation after 8-ton application of lime and the exchange capacity of experimental fields

FIELD	EXCHANGE CAPACITY	UNSATURATION AFTER 8-TON LIME APPLIED	UNSATURATION ON A CONTROL PLOT	RANK IN BUFFER CAPACITY BY 2 PER CENT CITRIC ACID
	m.e.	*per cent H*	*per cent H*	
E 4	34.0	33.1	43.0	1
E 5	32.0	29.6*	37.0	2
E 3	27.5	25.5	47.0	4
E 2	24.0	8.7	39.0	3
E 1	7.8	0	50.0	5

* 4-ton application of hydrated lime.

received 4 tons of hydrated lime, the effect of this amount being equal to that of 8 tons of the finely ground limestone applied to the other fields. The base capacity on field E 3 is 27 m.e. and the degree of unsaturation was lowered by 8 tons of lime from 47 per cent of 25.5. In field E 2 which has a base capacity of 24 m.e. a similar treatment decreased the unsaturation from 39 per cent to 8.7 per cent. On field E 1, where the exchange capacity is 7.8 m.e., 8 tons of lime completely saturated the exchange complex. In table 18 are presented the fields in order of their decreasing exchange capacity. It will be seen that the unsaturation on the plots receiving 8 tons of lime is lowered least upon field E 4.

Relation of unsaturation to crop response to lime

From time to time the degree of unsaturation has been suggested as a measure of lime deficiency. Recently Turner (28) working on sugar cane soils has published a report in which he suggests using the unsaturation as determined by the method of Page and Williams as a measure of the lime re-

quirement. By this he estimates that about three times the amount of lime necessary to bring the degree of unsaturation to 30 per cent is required to produce a maximum effect. He found 30 per cent unsaturation to be the limit in his so-called "good soils." Kappen also has set this value as the approximate one at which no great response to lime may be expected.

For a study of the problem the control plots from the 28 fields were used. The properties of the soils are shown in table 2. They were selected to show as wide a variation in the response of alfalfa to lime as possible. This range was from no response on such fields as D 6 to an increase in yield of 209 per cent on D 2.

The data from this study do not indicate a close relationship between the degree of unsaturation of the soil and the response to lime (table 19). They

TABLE 19

Increase in yield of alfalfa from lime and degree of unsaturation on 28 fields in southeastern Minnesota

GLACIAL OUTWASH			LOESS			GLACIAL DRIFT		
Field	Increase in yield	Percentage unsaturation	Field	Increase in yield	Percentage unsaturation	Field	Increase in yield	Percentage unsaturation
	per cent			*per cent*			*per cent*	
O 2	89	44.6	L 7	207	46.6	D 2	209	51.5
O 4	37	42.5	L 8	140	48.0	D 1	98	50.5
E 1	23	50.0	L 1	105	29.5	D 4	86	46.5
O 1	11	31.2	L 6	87	44.3	E 4	59	41.0
O 5	9	51.7	E 3	76	44.0	D 7	55	37.6
O 3	0	37.9	L 5	48	31.7	D 3	36	41.6
	..	....	L 10	46	40.4	D 8	24	14.6
	..	....	L 3	36	39.1	D 5	23	45.0
	..	....	L 2	22	39.4	E 5	19	37.0
	..	....	E 2	20	39.0	D 6	2	32.7
	..	....	L 4	17	50.9		...	....
	..	....	L 9	3	21.8		...	....

rather indicate that the relationship is general and that it holds more nearly in the more responsive soils. That is, of those which gave a definite response to lime only 4 out of 19 had an unsaturation of less than 39 per cent, and of those above 40 per cent unsaturated 14 of 16 showed decided responses. On the other hand the least unsaturated soil in the group, field D 8, with an unsaturation of 14.6 per cent, gave what may be termed a definite response though not a large one. In the soils which did not respond markedly the correlation between the crop behavior and the unsaturation is less. Of the nine soils in this group six had unsaturation of 37 per cent or above, two had 50 per cent.

To sum up, the unsaturation as an indication of crop behavior is of doubtful value on soils which show little unsaturation. Of those which show unsaturation of 40 per cent or above this study would indicate that about 85 per cent may be expected to give definite returns from lime.

SUMMARY

A study was made of the exchangeable bases in the soils of 28 fields in southeastern Minnesota. It included an investigation of the amount of replaceable bases, the degree of unsaturation, and the effect of lime upon the exchange complex and degree of unsaturation. The relationships existing between the unsaturation and the hydrogen-ion concentration and its relation to crop behavior with lime were also studied.

The soils were selected from experimental and demonstration fields of the University of Minnesota. From the demonstration fields only samples from the untreated plots were used, whereas from the experimental fields samples from plots receiving 1, 2, 3, 4, and 8 tons of lime as well as from the control plots were taken for analysis. The response of alfalfa to lime varied widely. The texture of soils ranged from loamy sand to silty clay loam.

The Gedroiz 0.05 *N* hydrochloric acid method was used to determine replaceable base, Bradfield's method using the NH_4OH—NH_4Cl buffer method for replaceable hydrogen, and the electrometric method, for the hydrogen-ion concentration.

The base capacity ranged from very low, 6.7 m.e., on the loamy sand to high, 48.0 m.e., on the silty clay loam. On all fields except the loamy sands and one silty clay loam the moisture equivalent was almost identical with the number of milliequivalents in the base capacity per 100 gm. of soil. Any marked textural change was noticeable in the base capacity.

The replaceable bases determined in these soils were calcium, magnesium, and hydrogen. The calcium was from three to six times as great as the magnesium and together they average 60 per cent of the total replaceable base. The magnesium appeared to be less affected by varying amounts of hydrogen present.

The content of replaceable base decreased from the surface downward. The decrease was about 2 m.e. of hydrogen and 2 of calcium in the second 6 inches and on soils developed on outwash and glacial drift there was a similar decrease in the second foot. On soils developed on loess there was somewhat less decrease below the first 6 inches. The magnesium remained more or less constant throughout the profile.

The degree of unsaturation in the surface soils varied widely but was generally high, averaging about 40 per cent. In most cases it was equally high in the second foot, but in the third foot there was a marked decrease.

The relationship of unsaturation to hydrogen-ion concentration was only general. Usually the more unsaturated soils had a lower pH. In the range of hydrogen-ion concentration from a pH of 5.8 to a pH of 6.2 there were wide variations in unsaturation. When the pH approached the neutral point the unsaturation was rather uniformly low.

An application of 8 tons of limestone an acre increased the total base capacity on four of the five experimental fields. Upon only one, E 2, did an amount

less than 8 tons produce any increase, but on this the 4-, 3-, and 2-ton rates were effective.

Limestone increased the replaceable calcium and magnesium somewhat in proportion to the amount applied, and in most cases the increase in calcium and magnesium exceeded the decrease in replaceable hydrogen. On fine textured soils it was necessary to apply at least 3 or 4 tons of finely ground limestone before any definite effect on the exchange complex could be observed, but on the coarse textured soil the effect of 1 ton was discernible.

The lime application decreased the degree of unsaturation more or less in proportion to the amount applied. On the loamy sand 8 tons of limestone caused complete saturation with a pH of 8.3.

The penetration of lime as observed by its effect upon the replaceable bases was not detected below the surface 6 inches except on the loamy sand. There it appears to have reached to the lower part of the second foot.

The buffer capacity of these soils was closely correlated with the exchange capacity. More lime was required to produce an effect on fine textured soils with high capacity than to produce an equal effect on coarse textured soils with a low exchange capacity.

The use of the degree of unsaturation as an indication of the crop response to be expected from lime is of doubtful value. If the soil is more than 40 per cent unsaturated the chances are that there will be an increase from liming in about 85 per cent of the cases. However there were a considerable number of soils having rather low unsaturations which gave quite as great a response to lime.

REFERENCES

(1) Bradfield, R. 1927 The use of electrodialysis in physico-chemical investigations of soils. *Proc. and Papers, First Internatl. Cong. Soil Sci.* 2: 264.

(2) Braezeale, J. F., and Magistad, O. C. 1928 Base exchange in orthoclase. *Ariz. Agr. Exp. Sta. Tech. Bul.* 24: 609.

(3) Gans, R. 1906 Konstitution der Zeolithe. *Jahr. Preuss. Landesault Bergakad* 27: 63.

(4) Gedroiz, K. K. 1908 Colloidal chemistry and soil science. *Zhur. Opytn. Agron.* (Russian), 2: —.

(5) Gedroiz, K. K. 1918 Contribution to the method of determining zeolitic bases in soils. *Zhur. Opytn. Agron.* (Russian), 19: 226.

(6) Gedroiz, K. K. 1923 The hydrochloric acid method for determining in the soil the cations present in an absorbed condition. *Soil Sci.* 16: 473.

(7) Harada, M. 1928 Exchangeable bases in soils. *Bul. Agr. Chem. Soc. Japan* 4: 41.

(8) Hissink, D. J. 1907 Deinvloed von verochillende zontoplossingen op het doorlatingsvermogen von den boden. *Chem. Weekbl.* 41: 1.

(9) Hissink, D. J. 1925 Base exchange in soils. *Trans. Faraday Soc.* 20: 551.

(10) Hoagland, D. R., and Christie, A. W. 1918 The chemical effects of CaO and $CaCO_3$ on the soil. Part I. *Soil Sci.* 5: 379.

(11) Joffe, J. S., and Mclean, H. C. 1926 Colloidal behavior of soils and soil fertility: II. The soil complex capable of base exchange and soil acidity. *Soil Sci.* 21: 181.

(12) Kappen, H. 1920 Ueber die Aziditätsformen des Bodens und ihre pflanzenphysiologische Bedeutung *Landw. Vers.* sta. 96: 277.

(13) KAPPEN, H. 1928 Der Sältigungszustand der Bodens und seine Bestimmung. *Fortschr. Landw.* 3: 1009.

(14) KELLEY, W. P., AND BROWN, S. MELVIN 1924 Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper 15.

(15) KELLEY, W. P., AND BROWN, S. MELVIN 1927 Base unsaturation in soils. *Proc. and Papers First Internatl. Cong. Soil Sci.* 2: 91.

(16) KERR, H. W. 1928 Nature of base exchange and soil acidity. *Jour. Amer. Soc. Agron.* 20: 309.

(17) LUNT, H. A. 1929 The vertical distribution of soil bases and acidity in some Illinois soils. *Soil Sci.* 28: 137.

(18) MAGISTAD, O. C. 1929 The use of artificial zeolites in studying base exchange phenomena. *Jour. Amer. Soc. Agron.* 21: 1045.

(19) MARTIN, J. C. 1927 Effect of crop growth on the replaceable bases in some California soils. *Soil Sci.* 27: 123.

(20) PARKER, F. W. 1927 Methods for the determination of the amount and avidity of exchangeable hydrogen in soils. *Proc. and Papers First Internatl. Cong. Soil Sci.* 2: 164.

(21) PARKER, F. W. 1929 The determination of exchangeable hydrogen in soils. *Jour. Amer. Soc. Agron.* 21: 1030.

(22) PARKER, F. W., AND PATE, W. W. 1926 Base exchange in soil colloids. *Jour. Amer. Soc. Agron.* 8: 470.

(23) PIERRE, W. H. 1931 Hydrogen-ion concentration in the soil solution and percentage base saturation as factors affecting plant growth on acid soils. *Soil Sci.* 31: 183.

(24) PIERRE, W. H. AND SCARSETH, G. D. 1931 Determination of the percentage base base saturation of soils and its value in different soils at definite pH values. *Soil Sci.* 31: 99.

(25) ROST, C. O. AND FIEGER, E. A. 1927 Effect of different kinds and amounts of liming materials upon the hydrogen-ion concentration of the soil. *Proc. and Papers First Internatl. Cong. Soil Sci.* 2: 45.

(26) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Effect of cropping with various fertilizers, manure, and lime treatments upon the exchangeable bases of plot soils. *Soil Sci.* 29: 371.

(27) THOMPSON, H. S. 1850 On the absorbent power of soils. *Jour. Roy. Agr. Soc. England* 11: 76.

(28) TURNER, P. E. 1930 The state of unsaturation of the soil in its relation to its field behavior and lime requirement. *Soil Sci.* 30: 349.

(29) WAY, J. T. 1850 On the power of soils to absorb manure. *Jour. Roy. Agr. Soc. England* 11: 313.

(30) WILSON, B. D. 1930 Exchangeable calcium and potassium in soils as affected by cropping and fertilization. *Soil Sci.* 29: 91.

EFFECTS OF STABLE MANURE AND CERTAIN FERTILIZERS ON THE MICROBIOLOGICAL ACTIVITIES IN VIRGIN PEAT[1]

S. C. VANDECAVEYE

Washington Agricultural Experiment Station[2]

Received for publication October 24, 1931

Better results have often been obtained by applications of animal manures to various types of virgin peat soils than by addition of like amounts of the same available plant-foods in the form of commercial fertilizers. This fact has favored the viewpoint held by those who maintain that the natural microbial activity in peat is low or totally absent and the most valuable effect of stable manure on peat is due to the microbes in the manure. Waksman's (17) review of the literature on the occurrence and abundance of microörganisms in peat bogs and his own work in this connection afford conclusive evidence that the microörganisms naturally present in peat soils play an important part in the transformation and liberation of plant-food. Those who maintain that the introduction of the bacterial flora of stable manure brings about greatly changed microbiological activities in soil have never offered really convincing proof of their contention. On the other hand, the many unsuccessful attempts to change soil flora by additions of cultures of certain microörganisms, or mixtures thereof, are evidence against such claims.

According to Tacke (12) the addition of stable manure to lowmoor peat has a favorable effect in promoting the liberation of available plant-food. Waksman (17) ascribes this effect to the increase in available carbon compounds with a suggestion that it might be due also to the microflora in the manure. That the liberation of plant-food in certain virgin peats supporting the growth of grasses, and therefore seemingly well supplied with available carbon compounds, is sometimes greatly stimulated by the addition of stable manure suggests a beneficial effect from the microflora introduced by the manure. However, Barthel and Bengtsson (1) concluded that microörganisms added with the manure are of no practical importance in normal mineral soils, since in their work sterilized manure acted in the same manner as unsterilized manure. In view of the divergence of opinion regarding this subject the work presented in this paper was undertaken in an attempt to ascertain the effect, if any, of the microflora of stable manure and also the effect of stable manure, wheat straw, and certain fertilizers on the microbiological activities in a virgin peat soil.

[1] The assistance of John Bixby and M. C. Allen in the microbiological analysis in this work is gratefully acknowledged.

[2] Published as Scientific Paper No. 199, College of Agriculture and Experiment Station, State College of Washington, division of agronomy, soils section.

EXPERIMENTAL PROCEDURE

The peat for this investigation was obtained from a virgin area near Everett, Washington, in T 29N, R 5E., Section 22, adjacent to a cultivated field in the same bog. It is a poorly decomposed, woody-sedge peat, reclaimed by diking about 15 years ago, and resembling that of the Monroe type described by Dachnowski-Stokes (4). Its reaction determined by means of the quinhydrone electrode in a suspension of one part of peat to five parts of distilled water was pH 4.3. Qualitative determinations for available plant-food in the surface 8-inch layer revealed only a trace of phosphorus with 0.2 *N* nitric acid and showed that this layer is low in replaceable calcium and potassium as determined by means of neutral salt replacement. Crop yields on the unfertilized peat under cultivation are poor and unprofitable but may be increased many times by applications of manure or phosphate fertilizers. Applications of nitrogen or potash fertilizers alone or in addition to phosphate fertilizers do not result in any marked increase in yield. It is evident that phosphorus is the limiting plant-food for crop production and must be supplied to this soil to obtain good crop growth.

In the fall of 1929 a representative quantity of this virgin peat taken from the surface 8-inch layer in the field was shipped to the laboratory, air-dried sufficiently to permit pulverization by rubbing, passed through a 16-mesh sieve, and thoroughly mixed. Under these conditions the moisture content was 18.1 per cent whereas that of the completely air-dried peat was 7.65 per cent. Unnecessary drying was avoided in order to prevent destruction of the microbial flora as much as possible. Water was added to the pulverized peat to make its moisture content equivalent to that of the field soil, which was approximately 200 per cent at optimum conditions for tillage operations and plant growth. A preliminary determination with a small sample of the pulverized material showed its water holding capacity had decreased as a result of drying and pulverization and it was found necessary to adjust its moisture content to 180 per cent instead of 200 per cent to obtain optimum moisture conditions. Following the addition of moisture the soil was allowed to stand for one week to assure uniform moisture distribution and as far as possible the normal resumption of the microbiological activities. For the first experiment six portions, each consisting of 1,000 gm. of moist peat, were thoroughly mixed with the various ingredients added for experimental purposes and were placed in wide-mouth bottles connected with an absorption train for carbon dioxide determinations. The carbon dioxide evolution was determined daily during the first week when microbiological action was greatest and less frequently thereafter, the interval between determinations being gradually increased until it was seven days beginning with the fourth week. Nitrate nitrogen, ammonia, and the number of fungi, actinomyces, cellulose decomposing bacteria, Azotobacter, and total bacteria were determined periodically. The moisture content of the peat was maintained at 180 per cent by addition of water when necessary. The treatment of the various lots of peat was as follows:

Number of sample	*Treatment per gm. 1,000 moist peat*
1	Check
2	0.7 gm. superphosphate(16.5 per cent)
3	7 gm. manure (air-dried)
4	7 gm. manure plus 0.7 gm. superphosphate
5	7 gm. sterilized manure plus 0.7 gm. superphosphate
6	7 gm. wheat straw plus 0.7 gm. superphosphate

The rate of application of these materials was equivalent to 600 pounds superphosphate, 10 tons of manure, and 3 tons of straw per acre based on the acre volume of the surface 7 inches of peat.

The manure was mediumly decomposed stable manure containing 2.04 per cent nitrogen on the dry basis. That used for sample 5 was sterilized in the autoclave at 15 pounds pressure for 2 hours on two successive days. Sufficient sodium nitrate was added to the finely ground wheat straw to make its nitrogen content equal to that of the manure.

At the end of 68 days the peat soil in all the bottles was inoculated with 25 cc. of a 1:5 suspension of Palouse silt loam known to contain an abundance of nitrifying bacteria and Azotobacter as well as other soil microbes. This was done to ascertain the effect of inoculation with the microflora of a fertile mineral soil on various microbiological activities in peat.

At the end of 129 days a second experiment was started to determine the effect of lime on nitrification and other microbiological activities in these variously treated peats. Because frequent sampling during the first experiment had decreased the volume of the soil in the bottles to a considerable extent it was considered advisable to combine the contents of two bottles into one previous to making lime applications. The arrangement was as follows:

Number of new samples	*Number of old samples combined*	*Treatment*
1	1 and 2	2 per cent $CaCO_3$ on dry peat basis
2	2 and 4	check
3	5 and 6	2 per cent $CaCO_3$ on dry peat basis

The calcium carbonate was thoroughly mixed with the peat, the latter being placed in the bottles, which were connected with a CO_2 collection train, and the same determinations were made as in the first experiment.

METHODS OF ANALYSIS

Sampling

Samples of peat for analysis were obtained by passing the contents of each bottle through a 6-mesh screen on a large cloth, mixing further by rolling the soil back and forth on the cloth before removing the required quantity for analysis. This method insures thoroughly mixed, representative samples, and at the same time, prevents the tendency toward possible anaerobic conditions developing in the lower part of the bottles. After the samples were

removed, the peat was returned to the bottles and packed by gently tapping the bottles on a table. The samples for the various analyses were spread evenly in a thin layer on paper and air-dried in the laboratory. This process of drying required only a few hours. All determinations were made on air-dry peat and the results calculated on the basis of dry peat.

Microbiological analysis

The direct microscopic method of Conn (3) was adopted for the determination of the total number of bacteria. Fungus spores and mycelia were not included in the counts.

The numbers of fungi, actinomyces, cellulose decomposing bacteria, and Azotobacter were determined as separate groups by plating on selective culture media. The fungi and actinomyces were determined from soil suspensions by the dilution plate method. Counts were made on duplicate plates and the numbers averaged for computation. The nutrient medium for fungi was potato extract agar adjusted to approximately pH 3.2 to 3.4 by addition of sterilized 0.1 *N* citric acid to the agar medium at the time the plates were poured. The actinomyces were grown on Waksman's (13) albuminate agar adjusted to pH 8. Silica gel plates 15 cm. in diameter were prepared as a substratum for the growth of Azotobacter and cellulose decomposing bacteria according to the method of Waksman (14). No duplicate plates were used for these organisms. Winogradsky's (18) nutrient solution for the growth of Azotobacter was used according to his direction, and Waksman's (14) nutrient solution and a sheet of filter paper superimposed upon the silica gel were used for the development of cellulose decomposing bacteria. The air-dried peat was spread evenly over the surface of these plates at the rate of 300 gm. per plate. All plates were incubated at 27°C. and the colonies of the respective groups of microörganisms counted at the end of the incubation period.

Chemical analysis

Total nitrogen was determined by the Kjeldahl method. Ammonia and nitrate nitrogen were determined on water extracts, nitrate nitrogen by the phenol-disulfonic acid method, and ammonia nitrogen by Nesslerization according to the official and tentative methods of the Association of Official Agricultural Chemists (8). The carbon dioxide collected in the NaOH solution of the absorption train was determined according to the method of Heck (7). Total carbon was determined by wet combustion using the method of Friedemann and Kendall (5). Unless stated otherwise the pH was determined by means of the quinhydrone electrode in a suspension of one part of soil in five parts of distilled water.

EXPERIMENTAL RESULTS

Before the different portions of peat were mixed with the various ingredients and placed in bottles the separate groups of microörganisms, carbon, nitrogen,

and reaction were determined on the moist peat and on the air-dried unsterilized manure in the manner described in the foregoing. The results of these determinations are given in table 1.

It is interesting to note that Azotobacter were present in this peat although its reaction was pH 4.3, which is much more acid than the arbitrary limits set by Gainey (6), who concluded that very few soils more acid than pH 6 contain Azotobacter. To make sure that their presence in this soil was not due to accidental contamination separate, fresh samples from the field were examined and similar results obtained. Unpublished data obtained in this laboratory show that the occurrence of small numbers of azotobacter in western Washington soils that are more acid than pH 5.5 is not unusual. Whether the activity of the Azotobacter in these acid soils has any practical significance remains to be determined, but the fact that they are present under these adverse conditions is not without interest.

TABLE 1

Determinations on original peat and manure based on dry material

DETERMINATION	PEAT	MANURE
Bacteria per gram	769,537,000	3,747,239,000
Fungi per gram	1,871,000	20,000
Actinomyces per gram	2,760	640,000
Cellulose decomposing bacteria per gram	92	350
Azotobacter per gram	18	None
Per cent N	1.93	2.04
Per cent organic C	37.10	37.34
P.p.m. NO_3	116.00	35.10
P.p.m. NH_3	243.30	Trace
pH	4.3	8.4

There was an abundance of microörganisms in the moist peat after it had been allowed to stand for one week, showing that microörganic life was active. Probably the drying and subsequent wetting of the soil had caused a temporary stimulation of the general microbiological activities and especially of the development of bacteria, since the latter suffered a sudden reduction soon after the experiment was started as will be noted later. In this connection it may be recalled that the bacteria were determined by direct microscopic counts, and therefore, their number would be expected to be considerably larger than if they had been determined by the plate method, for colonies counted on plates may result from groups of cells as well as from single cells. Furthermore, not all cells develop in the media used, because no one nutrient medium has ever been invented that is suitable for growth of all the different species of bacteria in the soil. Although results obtained by direct microscopic counts are not entirely free from criticism, nevertheless, they probably give a more accurate index of the actual number of bacteria in soil than do plate counts.

It is noteworthy to observe the impressive number of bacteria and the abun-

dance of actinomyces and fungi in the air-dried, unsterilized manure. The rate of application of this manure was equal to 1.93 per cent of the dry weight of peat. Thus the actual numbers of the various microörganisms added to the peat by means of unsterilized manure comprised approximately 73,460,870 bacteria, 392 fungi, and 12,389 actinomyces per gram of dry peat. This is an appreciable increase which should be reflected in subsequent microbiological analyses during the course of the experiment if the introduction of the microflora of the manure has any marked effect upon the microbiological activities in the peat.

TABLE 2

Carbon dioxide evolution

Expressed in mgm. of carbon per 100 gm. dry peat

DAYS	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6
1	10.5	9.5	17.0	14.7	21.5	22.2
2	12.7	13.3	19.8	19.5	23.0	28.2
3	11.4	10.3	12.8	14.8	14.3	19.7
4	9.7	9.3	12.5	13.3	13.9	15.8
5	10.9	11.9	12.8	12.9	11.2	12.9
6	9.8	9.3	11.3	11.2	11.8	12.5
8	18.7	19.5	22.7	23.5	24.8	24.7
11	29.5	30.7	36.3	38.0	39.4	39.8
14	25.5	27.0	32.8	32.2	33.5	33.3
19	36.8	44.4	44.2	46.7	45.3	40.3
26	48.3	58.8	62.0	67.5	65.5	60.8
33	34.1	36.8	38.2	37.5	37.2	39.4
40	37.3	44.0	55.5	53.7	52.7	59.0
47	47.5	55.8	64.3	68.2	64.3	90.3
54	45.8	48.3	64.6	68.0	54.8	82.5
61	16.8	39.2	64.0	59.8	51.0	63.5
68	39.4	36.5	61.4	48.9	45.8	44.8
75	36.4	33.6	56.0	39.6	40.4	31.3
82	30.2	29.4	47.6	38.3	33.9	26.3
89	30.8	40.4	47.9	38.1	28.4	27.6
103	37.6	35.7	53.9	40.6	47.5	35.7
Total.....	579.7	643.7	837.6	787.0	760.2	810.6

Experiment 1

To acquire a more comprehensive conception of some of the changes taking place in the peat as a result of the various treatments the author measured the total microbiological activities by the carbon evolved as carbon dioxide as well as by the changes in ammonia and nitrate nitrogen and the changes in numbers of the various groups of microörganisms as specified in the experimental procedure. Most of these changes were expected to take place most rapidly during the early part of the experiment, at least in the soils to which organic residues had been applied. For this reason carbon dioxide determinations and

microbiological analyses were made frequently during this period and less frequently later. The results of the carbon dioxide determinations are given in table 2. From a consideration of the total amounts produced by the variously treated peats it may be noted that the application of superphosphate to

TABLE 3

Total bacteria per gram of dry peat

(Last three figures omitted)

DAYS	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6
0	769,537	769,537	769,537	769,537	769,537	769,537
4	263,562	405,105	745,133	587,321	496,213	322,132
8	405,105	388,835	377,447	328,640	427,882	271,697
26	514,109	614,979	383,955	369,313	483,198	601,963
61	569,425	458,793	361,177	436,017	515,736	357,924
103	571,051	509,228	358,660	383,955	649,144	439,271
Average...	464,504	475,388	445,274	421,049	514,435	398,597

TABLE 4

Fungi and actinomyces per gram of dry peat

(Last three figures for fungi numbers omitted)

DAYS	FUNGI IN SAMPLES						ACTINOMYCES IN SAMPLES					
	1	2	3	4	5	6	1	2	3	4	5	6
0	1,871	1,871	1,871	1,871	1,871	1,871	2,760	2,760	2,760	2,760	2,760	2,760
4	6,992	4,600	6,348	7,452	7,636	3,864	9,200	5,520	9,200	3,680	7,360	10,120
8	4,048	3,220	5,152	2,024	4,140	3,036	13,800	8,280	11,040	11,960	4,600	15,640
14	7,084	1,978	2,539	1,297	4,784	.....	276	920	1,012	.....	736	644
19	3,680	3,772	1,656	1,306	1,417	1,536	1,012	1,196	1,288	1,656	3,036	1,656
26	1,481	1,886	1,306	1,444	1,260	1,564	3,220	4,784	4,232	3,864	2,208	.....
33	2,475	1,914	1,904	2,107	2,061	1,950	3,772	4,048	7,084	5,428	1,840	1,012
40	2,079	1,343	1,592	1,150	1,205	1,205	2,668	6,164	7,084	4,324	3,404	7,820
47	1,960	1,573	1,628	1,665	1,334	1,766	4,968	2,576	2,300	3,680	2,116	3,956
54	2,042	2,355	1,518	1,509	2,052	1,233	9,016	6,164	13,892	7,728	9,660	6,256
61	1,463	1,619	994	736	1,380	1,325	13,892	10,488	8,740	.....	12,880	10,672
68	1,527	1,776	1,352	1,417	1,444	828	7,360	18,216	16,744	6,256	15,824	6,624
75	1,408	764	1,021	837	1,187	828	10,396	6,256	4,600	6,532	13,984	6,900
82	1,592	1,104	1,978	1,196	883	1,822	7,636	6,900	12,144	3,496	10,672	9,936
89	1,122	1,058	1,527	782	948	1,923	10,304	7,820	8,188	3,864	7,176	9,660
103	1,187	938	322	460	644	1,095	.....	.....	.....	.....	.....	.....
Average..	2,676	1,993	2,056	1,692	2,158	1,713	6,966	6,381	7,682	5,206	6,821	6,992

sample 2 stimulated the evolution of CO_2 slightly, whereas the application of manure to samples 3, 4, and 5 and of wheat straw to sample 6 caused a marked increase in CO_2 production. As would be expected, this increase was greatest during the first dew days of the experiment, as represented graphically in figure

2 for treatment 6. Although the shape of the carbon curve would be similar for all treatments, the high points in the curve would be considerably lower in treatments 1 and 2 where no manure or straw was applied than in the samples that had received manure or straw. Available carbon and nitrogen compounds appeared to be the controlling factors, since the amount of CO_2 produced in the peat treated with straw compared favorably with that of the peats treated with stable manure. No significant difference in CO_2 production existed as a result of sterilization of the manure.

The numbers of total bacteria, fungi, actinomyces, cellulose decomposing bacteria, and Azotobacter determined at each sampling are given in Tables 3,

TABLE 5

Cellulose decomposing bacteria and azotobacter per gram of dry peat

DAYS	CELLULOSE DECOMPOSING BACTERIA IN SAMPLES						AZOTOBACTER IN SAMPLES					
	1	2	3	4	5	6	1	2	3	4	5	6
0	92	92	92	92	92	92	18	18	18	18	18	18
4	0	46	202	83	0	9	..	..	..	..	..	..
8	0	64	55	74	28	55	..	..	..	..	..	..
14	9	28	0	55	18	92	9	18	9	9	18	9
19	202	110	92	55	0	175	..	..	..	..	..	..
26	37	18	110	147	129	18	..	..	..	..	..	..
33	0	28	83	193	166	0	..	..	..	..	..	..
40	37	83	74	166	156	0	..	..	..	..	..	..
47	55	23	74	51	97	92	..	..	..	..	..	..
54	14	23	28	14	28	32	..	..	..	..	..	..
61	110	147	74	156	239	9	..	..	..	..	..	..
68	230	74	120	386	175	46	..	..	..	..	..	..
75	9	37	55	92	74	18	0	9	9	9	18	0
82	83	74	83	92	46	46	..	..	..	..	..	..
89	37	28	37	55	92	74	28	0	0	0	0	28
103	...	...	...	...	...	...	0	0	37	0	0	28
Average...	59	56	78	116	89	48	11	9	15	7	11	17

4, and 5. The most striking feature in these data is the sudden decline in numbers of bacteria in contrast with an equally sudden increase in numbers of fungi and actinomyces during the first 4 days of the experiment. The numbers of fungi remained relatively high for 2 weeks and gradually declined thereafter. The rapid increase in numbers of actinomyces continued for 8 days but was followed by a sudden drop and at the end of 3 weeks by a general but fluctuating rise reaching a second high peak at approximately 60 days. The numbers of cellulose decomposing bacteria and especially of Azotobacter were too small to have any significant bearing upon the results.

Apparently the large number of bacteria present at the time the experiment was started was the result of an abundant supply of readily available nutrients brought about partially by pulverization, but more especially by the drying

and subsequent wetting of the peat. This excessive food supply was soon exhausted, thereby causing the sudden drop in numbers of bacteria. The fungi and actinomyces, which are known to be capable of utilizing the more complex carbonaceous compounds to secure their energy, were not affected by the depletion of the readily available nutrients but were abundantly supplied with food suitable for their needs and therefore multiplied rapidly in proportion to the amount of food available. These results make it appear that the bacterial flora in this peat was able to compete successfully with the fungi and actinomyces as long as the readily available nutrients were present in abundance, and lead to the suggestion that bacteria as well as fungi take a prominent part in the decomposition of the readily available carbonaceous compounds in the organic matter.

Judging from the number of bacteria found on the fourth day of the experiment it seems that relatively few of the 73,460,870 bacteria added per gram of dry matter in samples 3 and 4 by means of unsterilized stable manure had survived, and even this effect was only temporary in nature, as in subsequent determinations the number of bacteria in these two samples and in the others was similar. A general analysis of the data relative to separate groups of microörganisms at each determination and comparison of these with the average number of each group throughout the experiment and with the total amount of carbon dioxide evolved as a result of each treatment clearly indicate that the microflora in the stable manure added to this virgin woody-sedge peat had no significant effect upon either the number of microörganisms or their activities. The results obtained from the samples treated with unsterilized manure, sterilized manure, and wheat straw in addition to superphosphate are comparable, as may be seen in figure 1. Naturally, the decomposition of wheat straw and manure could hardly be expected to proceed in exactly the same manner because there are distinct differences in the composition of the nitrogenous and carbonaceous compounds in the two substances. According to Waksman and Diehm (15), the chemical complexes of the animal excreta, which usually make up a large part of stable manure, have been modified materially by passage through the digestive tract of animals and therefore the excreta have been enriched in lignins and proteins. It is shown in figure 1 that the numbers of bacteria, and fungi, at the beginning of the experiment were lowest in the straw treatment. The average numbers of bacteria as given in table 3 for these three samples was also lowest in the straw treatment, but the average number of actinomyces and the total microbiological activities as measured by the liberation of CO_2 were greatest, so that the sum total of the microbiological activities for these three treatments may be considered to be comparable. Evidently the effect produced by these organic residues was due to their available carbon and nitrogen compounds. Barthel and Bengtsson's (1) results obtained from the addition of unsterilized and sterilized stable manure to mineral soil and those obtained here are similar, and their contention that the microörganisms added with the manure are of no practical importance

in the decomposition of organic matter in normal soils was substantiated in this experiment in so far as virgin peat is concerned.

Nitrate nitrogen and ammonia were determined regularly at each sampling and the results are summarized in table 6. It may be observed that with the

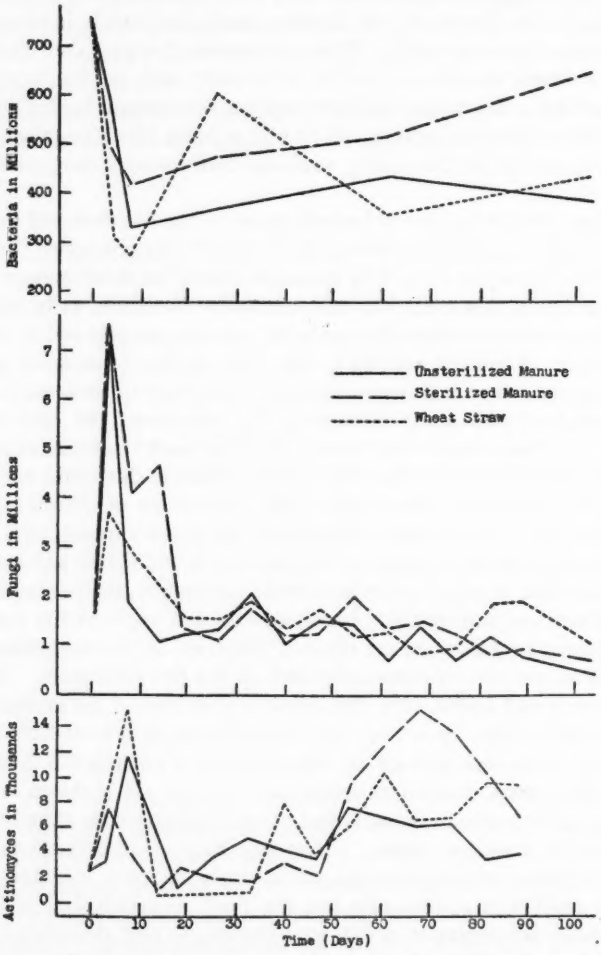


FIG. 1. BACTERIA, FUNGI, AND ACTINOMYCES IN PEAT TREATED WITH UNSTERILIZED MANURE, STERILIZED MANURE, AND WHEAT STRAW IN ADDITION TO SUPERPHOSPHATE

possible exception of sample 6, nitrification was rather slow. The maximum amount of nitrate nitrogen accumulated at any one time was 80 parts NO_3 per million parts of dry peat whereas the average accumulation of NO_3 dur-

ing the entire course of the experiment was only 20 p.p.m. The results of Sievers and Holtz (11) show that under similar conditions the accumulation of nitrate nitrogen in fallow, mineral soil containing less than one-tenth as much total nitrogen as the peat was approximately twice the amount liberated in peat during the same period of time. This indicates that nitrification in the peat soil proceeded slowly considering the abundance of ammonia accumulated and, therefore, available at all times for nitrification by the nitrifying bacteria. The exception in sample 6 may be accounted for in part at least by the nitrate nitrogen added with the straw, as its original total nitrogen content, which was 0.25 per cent, was increased to equal that of the manure by addition of $NaNO_3$. Since certain types of microörganisms are able to carry on their

TABLE 6

NO_3 and NH_3 in p.p.m. based on dry peat

DAYS	SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4		SAMPLE 5		SAMPLE 6	
	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3
0	94.3	197.8	94.3	197.8	94.3	197.8	94.3	197.8	94.3	197.8	94.3	197.8
4	99.8	259.7	108.1	249.5	97.0	187.6	83.2	187.6	97.0	218.1	266.2	187.6
8	33.0	196.5	37.2	196.5	37.2	186.4	45.5	206.6	35.8	175.4	137.7	180.9
14	85.1	166.8	106.4	166.8	79.8	166.8	79.8	155.2	95.7	161.9	319.1	161.9
19	169.2	269.2	143.6	288.0	174.4	288.0	160.0	280.8	150.0	280.8	400.0	327.4
26	132.7	49.8	172.6	137.2	146.0	158.2	132.7	149.3	139.4	141.6	398.2	141.6
33	142.7	280.9	129.1	203.9	129.1	267.3	129.1	280.9	122.3	280.9	353.3	229.9
40	147.7	302.0	134.2	302.0	134.2	335.6	134.2	302.0	134.2	302.0	362.4	318.8
47	140.1	382.2	140.1	406.6	133.8	238.9	133.8	274.9	133.8	251.6	369.4	238.9
54	132.1	260.0	132.1	283.0	132.1	271.5	119.5	307.1	122.6	271.5	339.6	235.9
61	133.3	272.7	157.6	318.2	145.5	272.7	151.5	272.7	157.6	296.0	424.2	250.5
68	109.8	343.5	109.8	274.4	115.8	252.0	109.8	297.8	115.8	274.4	341.5	182.9
75	107.0	424.5	113.2	401.5	107.0	471.7	119.5	471.7	116.3	354.3	301.9	388.9
82	90.0	217.6	90.0	144.7	90.0	265.8	96.5	252.9	99.7	241.2	283.0	217.6
89	100.3	376.2	94.0	282.1	94.0	282.1	87.8	235.1	99.2	212.1	288.4	188.1

activities with ammonia as a source of nitrogen, it is likely that only a part of the nitrate nitrogen added with the straw was required for the microbiological activities and the remainder was recovered in subsequent analyses.

The addition of either sterilized or unsterilized manure and of superphosphate did not result in any appreciable increase in accumulated nitrate nitrogen. Unless some indirect effect on nitrification occurred following the introduction of the microflora of the manure, accumulation of nitrate nitrogen as a result of the addition of the manure or of the wheat straw could hardly be expected during the course of the experiment, for, according to the work of Sievers and Holtz (10), applications of organic residues containing less than 2.25 per cent nitrogen to soil do not result in nitrate nitrogen accumulation during a similar period of time. The fact that large quantities of ammonia were present in the peat at all times regardless of treatment suggests that the slow

rate of nitrification was due either to the relative inactivity of the nitrifying bacteria or to a deficiency in their number. It will be recalled that on the sixty-eighth day of the experiment 25 cc. of a 1:5 suspension of Palouse silt loam known to contain an abundance of nitrifying bacteria was added to each bottle. This inoculation failed to stimulate nitrification, as may be concluded from the data in table 6. In fact, an actual depression in accumulation of nitrate nitrogen occurred toward the end of the experiment but this was probably due to dentrification. Although the inoculation of the peat with a soil suspension introduced numerous microörganisms other than nitrifying bacteria, the microbiological activities in terms of CO_2 evolution or numbers in the various groups of microörganisms were not affected.

Waksman and Stevens (16) called attention to the fact that in the decomposition of ordinary soil organic matter the ratio of carbon liberated as CO_2 to nitrate nitrogen accumulated as nitrate is about 10:1. In their work with Everglade peats they found this ratio to be entirely different, or 1.3:1 for sedementary peat, showing that in peat soil there is a rapid accumulation of nitrate nitrogen in comparison with the amount of carbon liberated as CO_2. In later work the same authors (17) observed that different ratios existed in different peats, some of them much wider than the one suggested for ordinary soils. The ratio between carbon evolved as CO_2 and nitrogen accumulated as NO_3 and NH_3 in woody-sedge peat in this experiment fluctuated considerably at various times, but at the end of the experiment proved to be about 17:1 in the untreated peat, 33:1 in the peat treated with unsterilized manure, and 37:1 in the peat treated with straw. The addition of sodium nitrate to sample 6 did not alter this relationship to any marked extent. This shows that available nitrogen probably was not deficient in this soil, but that the carbonaceous compounds were either resistant to decomposition or the reaction and possibly the calcium content of the soil were unfavorable for the promotion of rapid decomposition of these compounds. When large amounts of carbonaceous plant residues low in nitrogen are applied to soils likewise low in nitrogen very little or no accumulation of soluble nitrogen occurs until the decomposition of the carbonaceous organic residue is well advanced. Therefore, it appears the ratio between carbon evolved as CO_2 and soluble nitrogen accumulated in the soil is a variable function changing with the nature and quantity of carbonaceous compounds as well as with the nature and quantity of the nitrogenous compounds in the soil, other things being equal. For this reason Bedford's (2) computation of microbial activities in soil on the basis of organic matter content is not applicable in all cases. It would seem that the degree of inverse relation he observed between the number of microbes per gram of organic matter and the percentage of organic matter in the soil depends upon the nature of its carbonaceous compounds as well as upon the amount of organic matter. Likewise the inverse relationship he found between bacterial numbers per gram of organic matter and the total organic matter in a given quantity of soil is not strictly applicable unless it is correlated with the nature of the organic matter.

Attention has already been called to the fact that crop production in this woody-sedge peat is poor unless some available phosphorus is supplied by means of manure or commercial fertilizer. It might be presumed that since crops respond so generously to the addition of available phosphorus, microorganisms might react in a similar manner. In the peat treated with superphosphate there was only a slight increase in the liberation of carbon as CO_2, and no perceptible beneficial effect on nitrification or on the number of microorganisms in the various groups was observed. Since it is possible that soil acidity was adverse to normal microbiological activity a separate experiment was designed to throw more light on this point.

TABLE 7

Carbon dioxide and total numbers of bacteria in peat

(Last three figures for bacteria numbers omitted)

DAYS	C PER 100 GM. DRY PEAT IN SAMPLES			BACTERIA PER GRAM DRY PEAT IN SAMPLES		
	1	2	3	1	2	3
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm*
0	.....	.....	.....	292,853	297,728	309,116
7	370.0	50.7	358.9	395,343	358,016	395,343
14	138.7	51.3	121.1	432,854	351,416	476,690
21	151.9	57.5	146.4	.....	.....	.....
28	116.8	57.0	114.5	525,590	325,386	411,613
42	216.8	98.6	211.1	.....	.....	.....
57	267.5	49.3	274.0	540,139	356,297	505,974
79	273.2	112.5	287.2	.....	.....	.....
106	285.8	110.6	313.5	532.005	289,593	587,321
Total.....	1,820.7	587.5	1,826.7	453,131*	329,739*	447,676*
Carbonate C...	90.0	0.0	91.5	.....	.....	.....
Organic C.....	1,730.7	587.5	1,735.2	.....	.....	.....

* Average.

Experiment 2

The methods employed in this experiment were essentially the same as in the previous one and the object was primarily to ascertain the effect of lime on nitrification and reaction, and also on the microbiological activities previously considered. As stated in the experimental procedure the contents of two bottles were combined into one, making three portions, two of which received 2 per cent $CaCO_3$ and one of which, sample 2, served as a control. To make sure that an abundance of nitrifying bacteria and other members of the microflora of normal mineral soil be present, each portion of peat was reinoculated with 25 cc. of a 1:5 suspension of a fertile Palouse silt loam. The results of the experiment are reported in tables 7, 8, and 9. Attention is called to the fact that 20 days elapsed between the two experiments, and during that time

the numbers of bacteria and fungi had decreased considerably. This may have been partly because of a reduction in moisture content, although in experiments of this nature when no additional organic matter is supplied a gradual decline

TABLE 8

Fungi and actinomyces per gram dry peat

(Last three figures for fungi numbers omitted)

DAYS	FUNGI IN SAMPLES			ACTINOMYCES IN SAMPLES		
	1	2	3	1	2	3
0	616	212	442	3,680	2,760	4,600
7	672	460	432	21,160	13,800	17,480
14	552	1,288	460	28,520	8,280	26,680
21	552	92	653	30,360	5,520	22,080
28	580	3,036	497	20,240	5,520	21,160
42	920	1,748	368	12,880	4,600	14,720
57	736	1,656	350	7,360	3,680	11,040
79	847	1,472	405	10,120	4,600	12,880
106	773	1,196	350	13,800	6,440	14,720
Average...	694	1,240	440	16,458	6,133	16,151

TABLE 9

Cellulose decomposing bacteria, azotobacter, NO_3 and NH_3 and reaction of peat

DAYS	CELLULOSE DECOMPOSING BACTERIA PER GRAM DRY PEAT IN SAMPLES			AZOTOBACTER PER GRAM DRY PEAT IN SAMPLES			NO_3 AND NH_3 IN SAMPLES						pH—QUINHYDRON ELECTRODE IN SAMPLES			
							1		2		3					
	1	2	3	1	2	3	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3	1	2	3	Original peat
							p.p.m	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*				
0	14	14	14	18	18	9	131.5	65.0	280.0	57.0	168.0	64.0	4.3	4.5	4.4	4.3
7	9	14	5	74	9	46	.....	....	.....	.....	.....	.....	...	...	...	...
14	14	0	18	83	28	55	460.0	49.0	560.0	76.5	380.0	51.8	...	...	...	...
21	37	18	28	64	55	83	.....	....	.....	.....	.....	.....	...	...	...	....
28	74	41	87	37	46	74	.....	....	.....	.....	.....	.....	...	...	...	...
42	106	51	129	18	37	32	.....	....	.....	.....	.....	.....	...	...	...	...
57	78	37	133	28	0	51	.....	....	.....	.....	.....	.....	...	...	...	...
79	87	51	152	18	0	64	.....	....	.....	.....	.....	.....	...	...	...	...
106	97	37	124	32	0	74	833.5	17.4	611.9	551.4	940.1	110.0	6.6	6.3	6.7	6.5
Average...	57	31	85	41	21	54	.....	....	.....	.....	.....	.....	...	...	...	...

in numbers of microörganisms and a proportional reduction in the liberation of CO_2 usually occur as time progresses. That this actually took place in the woody-sedge peat may be noted by comparing the average numbers in the various groups of microörganisms and the total amounts of CO_2 liberated in

the untreated soil of the first experiment with those of the control soil in the second experiment.

In calculating the total amount of carbon liberated as CO_2 in table 7 the carbonate carbon in the lime was determined in the limed soils and the amount of this carbon evolved during the experiment was deducted from the totals. It is shown that the addition of lime to the peat caused a three-fold increase in the amount of carbon liberated as CO_2. Not all of this increase can be accounted for by increased numbers of microörganisms. Although liming resulted in nearly a threefold increase in numbers of actinomyces and in a marked increase in total bacteria the number of fungi was reduced approximately 50 per cent. The total average numbers of microörganisms comprising the various aerobic groups that were active in organic matter decomposition were actually less in the limed soils than in the untreated peat in the first experiment. If numbers of microörganisms as determined by the methods employed are a dependable criterion their activities as measured by CO_2 evolution must vary considerably according to environment. Evidently the addition of lime to woody-sedge peat stimulated the microbiological activities much more than the increase in numbers of microbes. Apparently the lime increased the working capacity of individual organisms and possibly this action was more favorable for the actinomyces and bacteria than for the fungi. This being the case it may be suspected that the major part of the increase in amount of carbon liberated was a result of the activity of actinomyces and bacteria, and not of fungi, as has been supposed generally.

Liming also increased nitrification materially but caused a decrease in the accumulation of NO_3 and NH_3 combined. More nitrate nitrogen and less ammonia nitrogen accumulated in the limed soils than in the control but the increase in the amounts of NO_3 was not equivalent to the decrease in the amounts of NH_3 thus pointing to the possibility that only a part of the accumulated NH_3 in the limed soils was nitrified and some of it was lost by volatilization.

The increased microbiological activity resulting from the application of lime caused a very marked change in the ratio of carbon evolved as CO_2 to soluble nitrogen accumulated. It will be remembered that in the first experiment this ratio was 17:1 for the untreated, 33:1 for the manured, and 37:1 for the straw treated peat. Sample 2 in the present experiment is comparable with the manured peats in the first experiment but its ratio of carbon evolved to soluble nitrogen accumulated is 19.7:1. That of the limed soils is 85:1 and 57:1 for samples 1 and 3 respectively. By increasing the availability of the carbonaceous compounds the ratio of carbon evolved to soluble nitrogen accumulated was widened beyond recognition, showing the extreme instability of this relationship.

The addition of lime did not affect the number of cellulose decomposing bacteria. Apparently woody-sedge peat is not a suitable medium for their development as their numbers remained small throughout the experiment.

Azotobacter seemed to be benefited by lime as their number, though small, seemed to remain rather constant in the limed soils. It is apparent that the inoculation with the Palouse silt loam suspension increased the Azotobacter population of the peat but as may be noted from the data in table 9 its effect gradually disappeared from the control soil to which no lime had been added. Both the cellulose decomposing bacteria and Azotobacter were too few in numbers to be significant in the results of this experiment.

It was expected that the addition of lime would decrease the acidity of the peat. The results of the pH determinations at the beginning and at the end of the experiment are recorded in table 9. For some obscure reason the pH of the control peat at the end of the experiment had increased nearly as much as that of the limed soils. Fortunately some of the original pulverized, moistened peat was placed in bottles which were stoppered with cotton plugs and stored in a separate room. The data show that the pH of this soil also had increased and was similar to that of the limed soils. Separate colorimetric pH determinations gave identical results. The decomposition of organic acids, which may take place in organic soils through good aeration, can hardly account for this great change in reaction. Since no logical reason can be offered for this phenomenon, the effects of lime on the microbiological activities in this soil cannot be attributed to changes in soil reaction.

DISCUSSION

The function of microörganisms in the transformation of organic matter in soil is a process of decomposition and synthesis. The rate of transformation depends upon many factors, chiefly moisture, temperature, aeration, food supply, and kind and number of microörganisms. The data presented in this paper show that under the conditions of the experiments food supply was of greater importance than were microörganisms. The microflora of the peat seemed to be adequate in numbers and in kind, because the introduction of the microflora of stable manure or of Palouse silt loam into the peat soil had no perceptible effect upon the number and kind of its microörganisms or their activities. Conversely, the food supply in the manure, consisting of readily available carbon and nitrogen compounds, greatly stimulated both numbers and activity of the microörganisms in the peat.

Bedford (2) mentioned the fact that the numbers of microörganisms of peat and mineral soils are wholly divergent when calculated upon the organic matter content of the soil. It has been pointed out in this paper that the number and activity of microörganisms are dependent upon the quantity of readily available carbonaceous and nitrogenous compounds in the organic matter as well as upon its total amount. Much of the organic matter in peat is extremely resistant to decomposition. The percentage of its total organic matter undergoing rapid transformation is so small that it is hardly comparable with that which is undergoing rapid transformation in mineral soils, especially in those cultivated mineral soils that are annually supplied with fresh crop residues or

manure. The microflora of peat may differ from that of mineral soils in many respects independent of the total organic matter of the soil. A comparison of the microbiological activities of the woody-sedge peat to which wheat straw and sodium nitrate had been added with those of a fertile Palouse silt loam is graphically expressed in figures 2 and 3. The data for the Palouse silt loam were obtained in this laboratory in a separate experiment to be reported in a subsequent paper. This mineral soil contained 3.1 per cent organic matter, 0.145 per cent nitrogen, and only a trace of nitrate nitrogen when the experiment was started. Its reaction was pH 6.9. As may be seen from table 1,

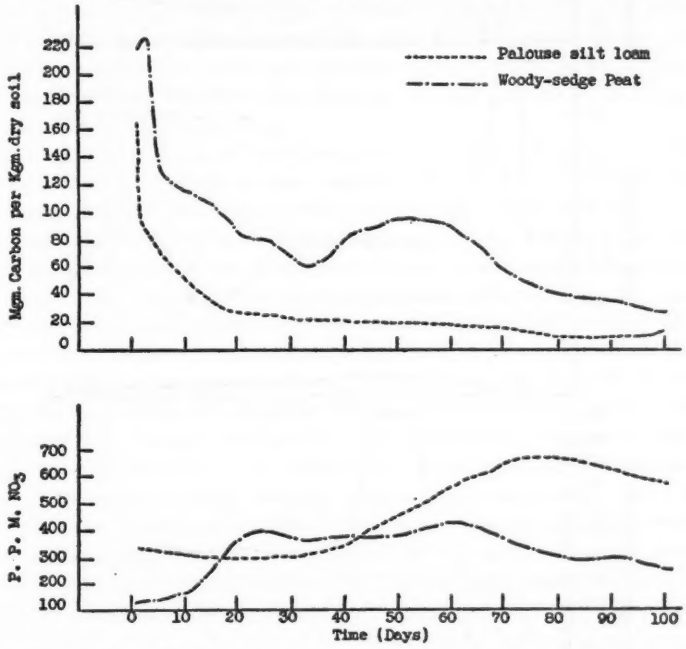


FIG. 2. CARBON DIOXIDE EVOLUTION AND NITRIFICATION IN PALOUSE SILT LOAM AND WOODY-SEDGE PEAT TREATED WITH WHEAT STRAW AND SODIUM NITRATE

the woody-sedge peat contained over 60 per cent organic matter, 1.93 per cent nitrogen, 21 p.p.m. NO_3, and its reaction was pH 4.3. Both soils received approximately the same percentage of wheat straw and sodium nitrate. The differences in microbiological activities between the two soils are obvious. The sum of these activities measured in CO_2 evolution was greater in the peat soil than in the mineral soil. The reverse was true for the amounts of nitrogen liberated as NO_3. The numbers of bacteria and actinomyces were much larger in the mineral than in the peat soil but the opposite was true for the numbers of fungi. The sum of the average number of bacteria, fungi, actinomyces, and

cellulose decomposing bacteria per gram of dry soil was nearly 800 million in the mineral soil, whereas it was less than 500 million in the peat. The smaller number of microörganisms in the peat liberated the greater amount of CO_2.

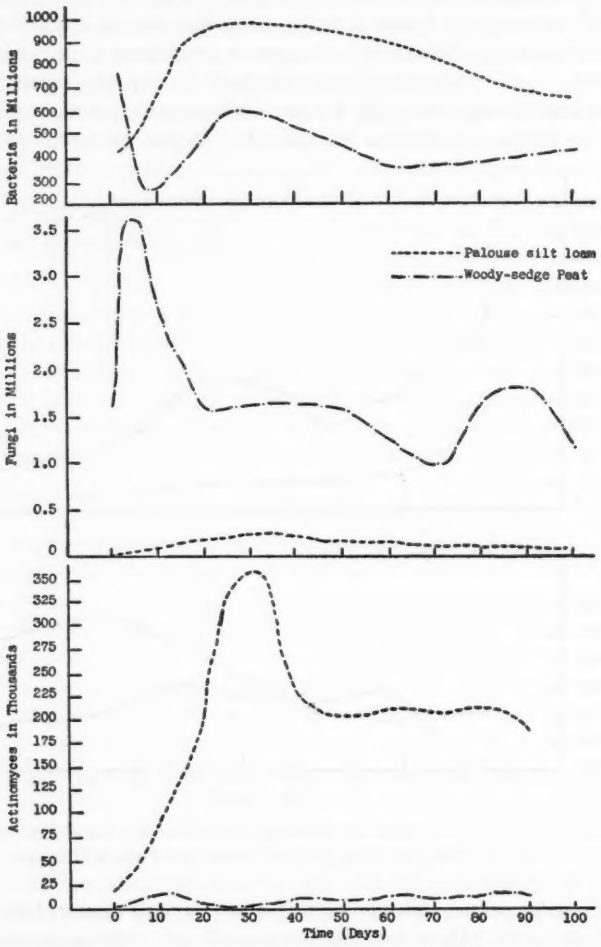


FIG. 3. BACTERIA, FUNGI, AND ACTINOMYCES IN PALOUSE SILT LOAM AND WOODY-SEDGE PEAT TREATED WITH WHEAT STRAW AND SODIUM NITRATE

The ratio of carbon liberated as CO_2 to the nitrogen accumulated as NO_3 and NH_3 was 37:1 for peat and 7:1 for Palouse silt loam. Marked differences occurred in the amounts of carbon liberated and in the numbers of bacteria, fungi, and actinomyces. These are variations existing between a mineral and

a peat soil, both receiving similar treatments and kept under identical conditions of aeration, moisture, and temperature. It is evident that the amount of organic matter, regardless of its resistance to decomposition or its composition, is inadequate as a means for computation of microbial activities in soil.

It has often been stated in the literature that a large part of the decomposition of organic matter in peat is a result of the action of fungi. Since fungi were much more numerous in the peat than in the mineral soil referred to it might be supposed, and it frequently is, that a large part of the carbon liberated in peat in excess of that in the mineral soil, as shown in figure 2, may be accounted for by the action of fungi. It must be remembered that the addition of lime to the peat caused a threefold increase in CO_2 production and simultaneously a 50 per cent decrease in numbers of fungi. This indicates that the comparatively large amount of CO_2 liberated from the peat cannot be explained on the basis of fungous activity.

Although the addition of lime stimulated CO_2 evolution it did not cause any increase in the sum of the average numbers comprising the various groups of microörganisms as determined in these experiments. Waskman and Stevens (17) and Shunk (9) observed a similar increase in CO_2 production following the addition of lime to peat, but Shunk found a simultaneous increase in the number of bacteria. It seems that the most important effect of the lime added to the woody-sedge peat was that of bringing about certain changes which caused an increase in those carbonaceous compounds that are readily available for decomposition by the soil microflora. Although the total number of microorganisms was not altered materially the relationship between groups of microorganisms was changed significantly. This relationship changed in the direction of that existing in the mineral soil, which presumably contained a large percentage of readily available carbonaceous compounds. Since both soils were well supplied with available nitrogen, it seems reasonable to suppose that the change in relationship in numbers between groups of microörganisms brought about by the addition of lime to peat was due primarily to an increase in readily available carbon compounds.

SUMMARY

A virgin woody-sedge peat was treated with unsterilized stable manure, sterilized stable manure, wheat straw, superphosphate, sodium nitrate, and lime, to study the effect of these substances on the numbers of various groups of microörganisms and their activities. The numbers of microörganisms were determined at regular intervals by means of direct microscopic counts and by counts of colonies developing on plates prepared with selective culture media. Their activities were ascertained periodically by determinations of carbon evolved as CO_2 and of nitrogen accumulated as NO_3 and NH_3. The addition of stable manure, or wheat straw to which sodium nitrate had been added to equal the nitrogen content of the manure, increased CO_2 evolution and also the numbers in the various groups of microörganisms, except those of the cellu-

lose decomposing bacteria and the Azotobacter. It also increased the accumulation of nitrates but not of ammonia.

The microflora of unsterilized stable manure had no perceptible effect opon the numbers in the various groups of microörganisms in the soil or upon their activities. It was indicated that the beneficial effect of stable manure on the microbiological activities of the woody-sedge peat was derived from the readily available carbon and nitrogen compounds in the organic matter of the manure. Stable manure and wheat straw gave comparable results.

The addition of superphosphate or sodium nitrate caused no material increase in the total number of microörganisms, or in numbers in the various groups of microörganisms, and had no marked effect upon their activities in the soil.

The addition of lime greatly stimulated the liberation of CO_2 but did not cause any marked increase in total numbers comprising the various groups of microörganisms. It seemed to benefit Azotobacter to the extent that their numbers remained constant in the soil. It was apparent also that it caused an increase in the percentage of readily available carbon compounds in the organic matter of the peat as shown by a change in relationship in numbers between groups of microörganisms in the direction of that existing in a fertile mineral soil.

The total numbers of microörganisms and the relationship of various groups of microörganisms in peat and in a mineral soil similarly treated are compared. It is indicated that the total number of microörganisms, the numbers in various groups, and their activities in peat and in mineral soil may vary in many respects.

REFERENCES

(1) Barthel, Chr., and Bengtsson, N. 1924 Action of stable manure in the decomposition of cellulose in tilled soil. *Soil Sci.* 18: 185–200.

(2) Bedford, R. H. 1929 A study of nitrate production in virgin soils of Alberta. *Sci. Agr.* 9: 391–399.

(3) Conn, H. J. 1929 Use of the microscope in studying the activities of bacteria in soil. *Jour. Bact.* 17: 399–405.

(4) Dachnowski-Stokes, A. P. 1930 Peat profiles in the Puget Sound Basin of Washington. *Wash. Acad. Sci.* 20: 193–209.

(5) Friedemann, T. C., and Kendall, A. I. 1929 The determination of carbon and carbon dioxide. *Jour. Biol. Chem.* 82: 45–55.

(6) Gainey, P. L. 1923 Influence of the absolute reaction of a soil upon its Axotobacter flora and nitrogen fixing ability. *Jour. Agr. Res.* 24: 907–938.

(7) Heck, A. F. 1929 A method for the determination of total carbon and also the estimation of carbon dioxide evolved by soils. *Soil Sci.* 28: 225–255.

(8) Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. 1924 Ed. 2: 24–84.

(9) Shunk, I. V. 1929 Microbiological activities in the soil of an upland bog in eastern North Carolina. *Soil Sci.* 27: 283–303.

(10) Sievers, F. J., and Holtz, H. F. 1922 The silt loam soils of Eastern Washington and their management. Wash. Agr. Exp. Sta. Bul. 166.

(11) SIEVERS, F. J., AND HOLTZ, H. F. 1926 The significance of nitrogen in soil organic matter relationships. Wash. Agr. Exp. Sta. Bul. 206.

(12) TACKE, BR. 1924 Untersuchungen über bakterielle Vorgange in verschiedenen Niederungsmoorböden. *Jahrb. Moork.* 13: 29–32.

(13) WAKSMAN, S. A. 1922 Microbiological analysis of soils as an index of soil fertility: II. Methods of the study of numbers of microorganisms in the soil. *Soil Sci.* 14: 283–298.

(14) WAKSMAN, S. A., AND CAREY, C. 1926 The use of the silica gel plate for demonstrating the occurrence and abundance of cellulose-decomposing bacteria. *Jour. Bact.* 12: 87–95.

(15) WAKSMAN, S. A., AND DIEHM, R. A. 1929 Chemical and microbiological principles underlying the transformation of organic matter in stable manure in the soil. *Jour. Amer. Soc. Agron.* 21: 795–809.

(16) WAKSMAN, S. A., AND STEVENS, K. R. 1929 Contribution to the chemical composition of peat: III. Chemical studies of two Florida peat profiles. *Soil Sci.* 27: 271–281.

(17) WAKSMAN, S. A., AND STEVENS, K. R. 1929 Contribution to the chemical composition of peat: V. The rôle of microorganisms in peat formation and decomposition. *Soil Sci.* 28: 315–340.

(18) WINOGRADSKY, S. 1925 Études sur la microbiologie du sol: I. Sur la méthode. *Ann. Inst. Pasteur* 39: 299–354.

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: VIII. FORMS AND FUNCTIONS OF WATER[1]

SANTE MATTSON

New Jersey Agricultural Experiment Station

Received for publication October 28, 1931

Water is associated in various forms with the colloidal materials of soils:

COMBINED WATER

First we have the constitutionally combined water of the hydrous oxides of aluminum, iron, and silicon and their hydrous compounds. This water can be driven off only by strong ignition. The best available data showing the relation of this water to the composition of soil colloids are found in the work of Robinson and Holmes (18). It is believed that a further systematic study in this direction would yield important information in regard to the constitution of the colloidal material, to its degree of hydrolysis, and to the relation of the latter to ion adsorption and exchange. The previously discussed isoelectric precipitates are therefore now being studied in respect to their combined water.

HYGROSCOPIC WATER

Next we have the surface attracted water or the hygroscopic water which is held by a powerful molecular attraction. This innermost film of water is subjected to a considerable compression, which has been estimated in the case of charcoal to a force equivalent to over 20,000 atmospheres (8). We may assume the heat of wetting to be a result of this compression. The compression is evident from the smaller apparent specific volume of colloids in water than in liquids like toluol and petroleum ether (16) in which the molecular attraction and the resulting compression are weaker.

The following figures for two of the soil colloids here studied are of interest. The figures are from the work of Anderson (1) and of Anderson and Mattson (2).

SOIL COLLOID	$\frac{SiO_2}{R_2O_3}$	HEAT OF WETTING PER GRAM	H_2O ADSORBED OVER 30 PERCENT H_2SO_4 PER GRAM COLLOID	SPECIFIC VOLUME IN WATER	SPECIFIC VOLUME IN TOLUOL	DIFFERENCE
		calories	*gm.*			
Sharkey	3.11	16.3	0.1605	0.368	0.387	0.019
Norfolk	1.60	7.6	0.0845	0.369	0.379	0.010

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

It is seen that the heat of wetting parallels the hygroscopicity. The differences in the specific volume in the two liquids indicate the volume contraction of the adsorbed water or rather the excess in the volume contraction of the water over that of the toluol. The figures are somewhat lower than the corresponding values for starch as given by Rodewald (19).

That the force of molecular attraction decreases rapidly as the distance increases is evident in various ways. Thus the surface tension of a film should show a decrease when the thickness of the film becomes less than twice the range of the molecular attraction. It was found by Rücker and Reinold (20) that for water there was no decrease in surface tension before the thickness of the film was reduced to $10\mu\mu$ ($= 1 \times 10^{-6}$ cm.). Again the vapor pressure of water droplets does not show an appreciable increase until their diameter falls considerably below 1μ. This indicates that the surface of a droplet of this dimension is to the molecule like a plane surface, since within the range of molecular attraction there is no effective curvature. Edser (5) states that the force of molecular attraction varies inversely as the 8th power of the distance.

The thing of interest in connection with our present subject is the quantity of water which is thus attracted to the surface of the colloid with the evolution of heat. The drier the colloid the greater is the quantity of heat liberated upon wetting. At what moisture content does the colloid cease to give off heat when wetted? The work of Rodewald (19) on starch showed the heat of wetting of this substance to be zero at a moisture content of 31.63 per cent, and Mitscherlich (15) found the heat of wetting of peat and of a heavy clay to approach zero at a moisture content of about 20 gm. of water in 100 gm. of dry soil. This moisture content is equivalent to the hygroscopicity of the materials. In soil colloids this varies with the composition and is in general higher the higher the ratio of silica to sesquioxides (2). The quantity of water thus attracted by molecular forces to the surface of colloids is therefore not very great, not nearly as great as the quantity of water that may, under certain conditions, be osmotically imbibed by the colloid.

What then is the order of magnitude of this, the hygroscopic film of water which is so tenaceously held by the particles? If we assume a uniform particle size we can calculate the ratio $r:r_1$ where r is the radius of the solid particle and r_1 the radius of the particle plus its layer of hygroscopic moisture. One gram of dry soil colloid, sp. gr. 2.65 occupies $\frac{1}{2.65}$ cc. $= 0.378$ cc. This would make a sphere with a radius

$$r = \sqrt[3]{\frac{0.378}{4/3\ \pi}} = 0.448 \text{ cm.}$$

If the hygroscopic moisture is 0.2 cc. per gram dry soil colloid, e.g., the approximate value for the Sharkey soil colloid, then our 0.378 cc. solid sphere would be covered with this water and we would have a 0.578 cc. sphere with a

radius $r_1 = 0.518$ cm. In 1 gm. of soil colloid there are billions of particles but if they were all spheres of uniform size the ratio $r:r_1$ would be the same, or 448:518. If, therefore, we knew the particle size we would know the approximate thickness of the film.

By ultramicroscopic count the Sharkey soil colloid, dispersed by ammonia, yielded an average particle radius, of 45$\mu\mu$ (2). If this were the ultimate size then the average thickness of the film would be about $52 - 45 = 7\mu\mu$. But by electrodialysis, by saturation with NaOH, and by diffusion through a Pasteur-Chamberland filter the author later estimated, by comparing the volume of floc of the Na-saturated Sharkey with the volume of floc of the ammonia treated colloid (11), a particle radius of 26$\mu\mu$. (The Na-saturated particles were not all visible in the ultramicroscope.) If we take this as the ultimate size of the particles then we find by the foregoing ratio a thickness of the film equal to about 4$\mu\mu$.

Although this estimate of the thickness of the hygroscopic moisture film is based on several assumptions it is significant that the order of magnitude is very nearly the same as that arrived at by P. Ehrenberg (6). Basing his conclusions upon theoretical considerations as well as upon a rich array of experimental data this authority fixes the thickness of the hygroscopic moisture film at 2.5$\mu\mu$ or equal to about 10 molecules of water. Mitscherlich accepts the thickness of the film as given by Ehrenberg and uses it as a basis for calculating the total surface of a soil (16).

The thickness of the film of molecularly attracted water $(r_1 - r)$ must therefore be considerably less than the radius of the particles. In the Na-saturated condition certain soil colloids swell and imbibe so much water that, on the same basis of calculation, the thickness of the water envelope is nearly twice the radius. That this very great but less powerful inbibition of water is due to osmotic forces will be shown later.

The expansion or swelling of a porous material resulting from the intake of the molecularly attracted water is manifested by great energy. Thus Rodewald (19) found that it required 2073 kgm. per cc. to prevent dry starch from swelling in the presence of water. Because of the loose structure of soils the swelling resulting from the intake of the molecularly attracted water is not so marked. The great force of expansion of dry wood when wetted is a familiar example of the energy of this form of swelling.

As to the nature of this innermost film of molecularly attracted water we have no definite knowledge. The molecules of water in this film occupy probably an oriented position as distinguished from the random distribution in the interior of the mass of water. The water adsorbed by molecular attraction must therefore possess different properties as compared to free water. It is more dense and must have a different viscosity or, indeed, be quite rigid like a solid, especially in the innermost layers. It does not freeze even at 70°C., as shown by the work of Bouyoucos (4). The dielectric constant is probably also different. The electrical polarity in this oriented layer of water molecules,

if known, would probably explain why air bubbles and all inert substances, which do not dissociate diffusible ions, become negative in water. By virtue of this polarity the distribution of the OH and H ions of the water may be such that the former will predominate within the adsorption film and thus impart a negative charge, not to the particles (or the air in the air bubbles) but to their surrounding film of adsorbed water whereas an excess of H ions charges the outside liquid to positive. The dissociation constant of water may even be different from that of free water, in which case the process of hydrolysis may be greatly modified.

CAPILLARY WATER

Apart from any molecular attraction or osmotic force (see the following) a certain quantity of water will be held in the fine capillaries of the soil or colloid by virtue of the surface tension. Since the water wets the soil with great energy and thereby covers each particle with a thin film and since the surface tension tends to reduce the surface to a minimum it is obvious that water will be pulled up against gravity and fill the finest capillary spaces.

The height h to which water will rise in a circular capillary may be calculated from the familiar equation:

$$\pi r^2 h\ g = T\ 2\pi r$$

where T is the surface tension in dynes per centimeter hence

$$h = \frac{2\,T}{r\,g} \text{ cm.}$$

The height to which water will rise against gravity varies therefore inversely as the size of the capillaries. The force with which water is held in the most minute capillaries is quite enormous. Thus Lebedeff (9) found that water could be removed from all the soils which he studied up to a centrifugal force equal to 18,000 times the force of gravity. Between 18,000 and 70,000 × gravity the moisture content remained almost constant and represented the molecularly attracted, or hygroscopic water, being about 6 per cent in the Sassafras silt loam and about 31 per cent in a clay soil. The last water to be removed by the centrifuge is probably somewhat subjected to the force of molecular attraction and is therefore not entirely free capillary water held by the surface tension alone.

The free capillary water which is held or lifted up in the capillaries solely by the force of surface tension must exert a contracting and a downward pull tending thereby to reduce the distances between the particles and oppose any tendency to swell. The function of the capillary water is therefore opposite to that of both the hygroscopic water and the osmotically held water, which cause the absorbent to swell. The energy of swelling due to the molecularly attracted water is so great that any opposition offered by the downward pull of the capillary water becomes insignificant. The energy of swelling due to

osmotic imbibition is rather small. The opposing force of the downward capillary pull is here more equally matched and keeps the osmotic swelling in check. Thus if a Na-saturated soil colloid in the process of imbibition is required to lift the water against gravity, as when placed in a funnel provided with a stem several feet long, the swelling is greatly reduced.

The study of the capillary forces in dispersed materials will show no definite relationship between the various factors unless a completely inert powder is used. In the case of reactive materials like soils which dissociate diffusible ions we shall encounter an osmotic imbibition. These osmotic forces will extend across the minutest capillaries and part way across the larger ones. The force by which the water is held or the height to which it is lifted is therefore by no means an expression of the capillary forces alone. Under certain conditions the capillary forces are altogether eliminated. The Na-saturated soil colloids not only completely fill all capillary spaces, by osmotic imbibition, thus destroying every meniscus, but their particles are pushed a considerable distance apart. The particles become suspended, so to speak, in the osmotically imbibed liquid, in cushions of their "micellar solutions." We shall now turn our attention to this form of water.

THE WATER OF OSMOTIC IMBIBITION

The various forms and functions of soil water discussed in the foregoing pages have long been more or less definitely defined and have been the subject of an extensive study by many investigators. This cannot be said about the water of osmotic imbibition, which forms the main object of our present study. Where this form of water has been recognized it is because it could not have escaped recognition, producing as it does in many instances the most conspicuous effects. The forces with which it is associated in the soil have never been accounted for nor have its functions ever been formulated. This may not have been possible without the conception of the soil colloidal micelle as presented in the preceding articles (12).

Soil colloids saturated with alkali cations have, because of their great swelling, been classed as lyophillic colloids as distinguished from the lyophobic behavior of the same materials when saturated with divalent cations (7). But no satisfactory explanation of this influence of the nature of the exchangeable ions has been given. It has been suggested that the imbibed water represents the water of hydration of the ions. But apart from the fact that the imbibed water is often much too great to be thus accounted for there are other reasons which make this explanation unacceptable. These will be brought out later.

The enormous swelling exhibited by certain samples of bentonite has been ascribed to a micaceous structure, a "one-dimensional" colloid. The bentonites and many of the soil colloids apparently contain plate-like crystals but it is difficult to see why this should be a necessary condition for swelling and other colloidal properties. As far as the surface is the controlling factor we

should expect a greater effect if the particles were reduced to colloidal dimensions in two directions, that is, if the platelets were cut into narrow bars, whereas the greatest effect would be produced by a "tri-dimensional" colloid, that is, by cutting the bars into cubes.

In the first of this series of articles it was explained how we may account for the swelling as an osmotic phenomenon (12). If the colloidal particles dissociate diffusible ions they will be surrounded by a swarm or atmosphere of these ions. The electrostatic attraction will prevent these ions from diffusing very far away from the surface of the particle which, through the dissociation, has become a highly multivalent ion complex of opposite charge. This means that the osmotic pressure will be higher near the surface of a particle than it is in the outside medium. The ion density in the micellar atmosphere appears to decrease rapidly with the distance from the surface. The osmotic pressure and the force with which water is imbibed are therefore much greater the lower is the water content of the gel. We shall show later that a definite relationship exists between the pressure and the water content.

A highly dissociated cation such as the Na ion must cause a greater swelling of a negative colloid than when the latter is saturated with a less dissociating ion like the Ca ion. This is well known to be the case. Further, the addition of electrolytes must, according to the Donnan equilibrium, suppress the swelling of the colloid. This suppression should be governed by the concentration and by the valence of the ions of the free electrolyte in the solution. This relationship was experimentally verified in the work referred to.

To avoid too much repetition we shall confine ourselves to the following diagrammatic presentation which the author has found useful in making clear the application of this theory to the colloidal micelle:

In figure 16 are shown two spheres representing a Na-saturated and a Ca-saturated micelle. The micelle consists of the colloidal particle or ion complex; the atmosphere of dissociated, diffusible ions; and the osmotically imbibed water. The relation between the size of the particles and the thickness of the layer of osmotically imbibed water, as shown in the figure, was calculated from the volume occupied by 1 gm. of the Na- and Ca-saturated Sharkey soil colloid after complete inbibition of water. The respective volumes were 7.25 and 1.86 cc. If we assume a specific gravity of 2.65 and that the particles are spherical and all of the same size, we get the relationship shown in the figure.

The very great imbibition of water by the Na-saturated colloid as compared to that of the Ca-saturated material is to be ascribed to a greater dissociation of the Na ions. This causes a greater osmotic pressure around the particles, which are therefore pushed further apart by the greater osmotic inflow of water.

The swelling of the soil colloid saturated with any cation will be at a maximum in the absence of free electrolytes. To illustrate how the free electrolyte causes a suppression of the swelling we shall choose a specific case and confine ourselves to the simplest effect, that of a uni-univalent salt.

Let v_i, figure 16, represent a small volume within the micellar solution of a

Na-saturated colloid and v_o an equal volume in the outside solution. Assume then that the concentration z of the micellar ions, i.e., ions dissociated by the particles, is such that there is an average of 12 ions in v_i. If there were no free ions in the dispersion medium (an ideal case never realized) then the osmotic pressure would be directly proportional to z and would be at a maximum.

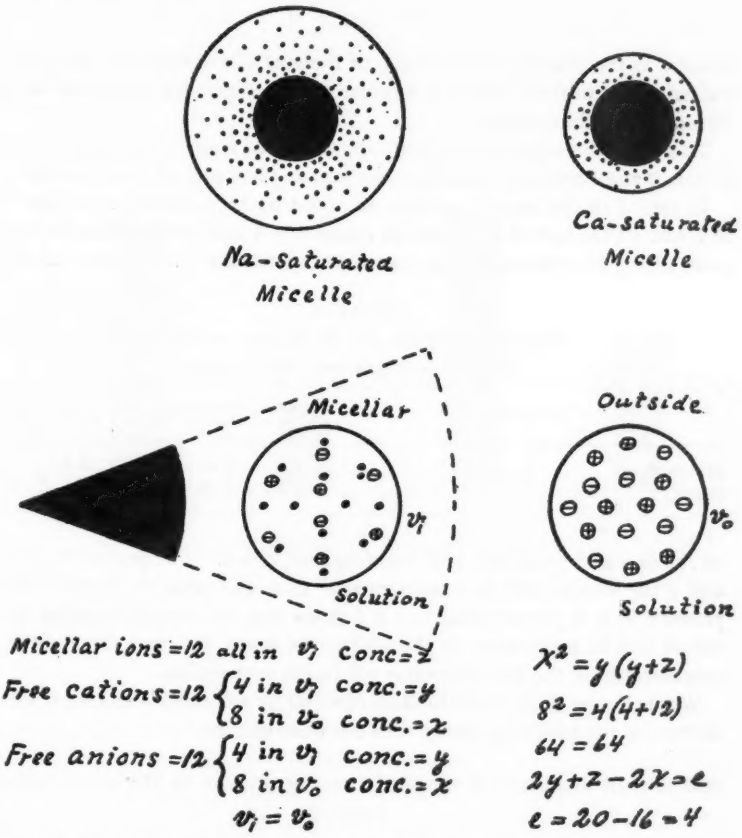

Na-saturated Micelle
Ca-saturated Micelle
Micellar
Solution
Outside
Solution
• Micellar ions = 12 all in v_i conc. = z
⊕ Free cations = 12 { 4 in v_i conc. = y ; 8 in v_o conc. = x
⊖ Free anions = 12 { 4 in v_i conc. = y ; 8 in v_o conc. = x
$v_i = v_o$
$x^2 = y(y+z)$
$8^2 = 4(4+12)$
$64 = 64$
$2y + z - 2x = e$
$e = 20 - 16 = 4$

FIG. 16. THE DONNAN DISTRIBUTION OF IONS BETWEEN THE MICELLAR AND THE OUTSIDE SOLUTIONS

Now let the total outside solution be equal to the total micellar solution so that v_o and v_i represent the same fraction of each and suppose that we add so much of a uni-univalent salt, e.g., NaCl, to the system that if equally distributed there would be 6 cations and 6 anions in v_o and an equal number in v_i, or together 12 ions of each kind in v_o and v_i. What will be the ultimate distribution

of the ions of the added salt at equilibrium and how will this distribution affect the difference in osmotic pressure between v_i and v_o?

According to the principle of a constant ion product the distribution must follow the Donnan equation, which, in application to the case here studied, demands that the product of the ions in v_i must equal the product of the ions in v_o thus

$$x^2 = y\,(y + z)$$

where x is the concentration of each of the ions of the salt in v_o and y is the concentration of these ions in v_i whereas z is the concentration of the Na ions dissociated by the complex.

To satisfy this equation the figure shows that at equilibrium there would be 4 cations and 4 anions of the added salt in v_i and 8 of each of these ions in v_o.

In regard to the second question we note that by summing up all the ions in v_i and all the ions in v_o we find an excess $e = 4$ ions in v_i whereas in the absence of any free electrolyte the excess ion concentration in v_i was equal to 12,

TABLE 87

Swelling of bentonite and the Sharkey soil colloid

Volume of gel in cubic centimeter per gram

TREATMENT	UNTREATED	ELECTRODIALYZED	Na-SATURATED	K-SATURATED	Ca-SATURATED
Bentonite	7.8	2.6	8.0	4.6	...
Sharkey	1.85	1.75	7.2	...	1.9

i.e., since x and y are then both equal to zero, $e = z$. The greater we make x and y the smaller will be e as compared to z, and since the excess osmotic pressure in v_i is proportional to e it follows that the osmotic swelling of the colloid will be suppressed by the addition of a salt and that the greater the concentration of the salt the greater will be the suppression.

We shall now study the imbibition of water by soil colloids and see if we can harmonize the foregoing theory with our observations.

THE OSMOTIC SWELLING AS GOVERNED BY THE NATURE OF THE EXCHANGEABLE CATIONS

That the swelling of bentonite and of soil colloids depends upon the nature and quantity of the exchangeable cations present rather than upon any particular structure was shown by the author some years ago (11). The swelling of the colloidal materials was studied as follows: Burettes were cut into lengths of 5-cc. capacities and the ends ground even. These tubes were placed in an upright position on a few pieces of filter paper on glass slides and held in that position by means of rubber bands. Half a gram of the material which had passed through a 50-mesh sieve was placed in each of the tubes and the latter

were then placed in a shallow dish containing sufficient distilled water to moisten the paper on which the material was resting. Water was imbibed through capillary rise and the volume occupied by the thoroughly wetted material was recorded as the swelling. The swelling of variously treated bentonite and the Sharkey soil colloid is shown in table 87.

By electrodialysis the bentonite lost its great swelling power. When the electrodialyzed bentonite was saturated with NaOH its power to swell was restored. In the K-saturated condition the swelling was intermediate between that of the Na-saturated and the H-saturated (electrodialyzed). The original bentonite contained no exchangeable divalent cations. The swelling of the bentonite is shown in figure 17.

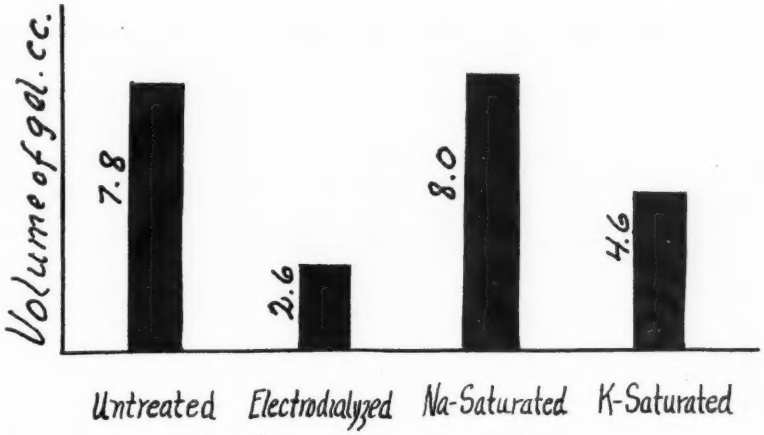


FIG. 17. THE SWELLING OF BENTONITE IN RELATION TO THE NATURE OF THE EXCHANGEABLE CATIONS

It was then found that if the Sharkey soil colloid was electrodialyzed and saturated with NaOH it developed a swelling power almost equal to that of bentonite.

The difference in the influence of Na and Ca upon the swelling of the Sharkey soil colloid is strikingly illustrated in plate 1. The electrodialyzed colloid was saturated with NaOH and $Ca(OH)_2$ in various proportion, a total of 0.80 m.e. per gram being taken. This quantity represents the exchange capacity of the colloid. Half-gram portions of the prepared samples were placed in a series of nine cylinders and allowed to imbibe water as described. The relative proportions of the two cations is shown in the figure where 100 represents full saturation.

The volume occupied by 1 gm. colloid after complete imbibition increased from 1.86 cc. of the Ca-saturated colloid to 7.10 cc. at full Na-saturation. A marked increase in swelling seems to take place after 20 per cent of the ex-

changeable Ca has been displaced by Na. This increase in swelling was accompanied by an increase in dispersibility and in the negative charge of the particles as shown in a previous publication (11).

OSMOTIC SWELLING AND THE CATION EXCHANGE CAPACITY

A very fundamental relationship was then observed. When NaOH was added in small increments to various electrodialyzed soil colloids it was found

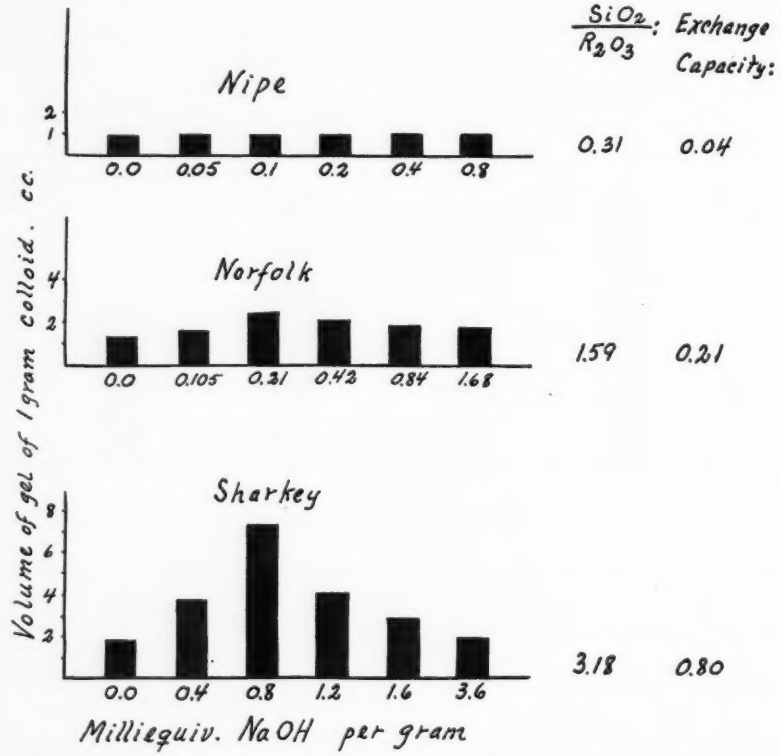


FIG. 18. THE RELATION BETWEEN SWELLING, COMPOSITION, AND EXCHANGE CAPACITY

that the swelling increased to a certain maximum and then again decreased. In all cases the swelling was at a maximum when the quantity of NaOH added was equal to the exchange capacity of the colloid. An excess of free electrolyte suppressed the swelling. It was further observed that the maximum swelling the colloid attained depended upon the cation exchange capacity. The higher this capacity the greater was the swelling and vice versa. Lateritic soil colloids possessing a very low cation exchange capacity show practically no increase in swelling in the Na-saturated condition. (The capillary spaces be-

tween the particles are evidently sufficient for the slight osmotic imbibition in these materials.) In figure 18 are shown the volumes occupied by the gel of 1 gm. colloid (110°C. basis) to which various quantities of NaOH have been added. The figure includes three soil colloids representing low, intermediate, and high cation exchange capacities.

Although the figure shows the differences most clearly, table 88 will be useful in showing (*a*) the volumes occupied per gram by the powdered (50-mesh), air-dry, electrodialyzed colloids after gentle tamping; (*b*) the volumes occupied by the gels per gram colloid in the electrodialyzed condition; and (*c*) the volumes of the gels per gram colloid when saturated with NaOH to the extent of their exchange capacities.

The experiment shows an unmistakable relationship between the power of soil colloids to adsorb and exchange cations and their power to imbibe water. The Nipe colloid with the very low exchange capacity of 0.04 m.e. per gram, showed practically no tendency to swell. Undoubtedly some water is osmotically imbibed even by this colloid but where the imbibition is very small it will be accommodated by the spaces between the particles in the porous mass of the material.

TABLE 88

The relation between exchange capacity and swelling

COLLOID	EXCHANGE CAPACITY	VOLUME PER GRAM AIR-DRY COLLOID	VOLUME OF GEL PER GRAM ELECTRO-DIALYZED COLLOID	VOLUME OF GEL PER GRAM Na-SATURATED COLLOID
	m.e.	*cc.*	*cc.*	*cc.*
Nipe	0.04	0.90	0.92	0.92
Norfolk	0.21	1.04	1.42	2.30
Sharkey	0.80	1.12	1.75	7.20

THE SUPPRESSION OF THE SWELLING BY ELECTROLYTES

It was shown in section I of this series (12) that, according to the osmotic equation deduced from the Donnan equilibrium, the swelling must be suppressed by the free electrolyte and that this suppression is governed wholly by the concentration and by the valence rule as explained. The swelling will also be suppressed, independently of any free electrolyte, whenever a highly dissociating cation (in a negative colloid) is displaced by a slightly dissociating cation. In this relation the Hofmestier series (which is governed by the specific nature of each ion and not alone by the valence) becomes manifest. Thus the swelling will be suppressed when Na is displaced by K and K by Ca.

We have seen that the Al and Fe ions will displace the exchangeable cations and that the complex thus formed has suffered a decrease in exchange capacity. The Al and Fe ions are not again displaceable by the neutral salt treatment

(13). This shows that these ions undergo very slight dissociation by the complex. Their introduction into the complex amounts to an artificial lateriza-

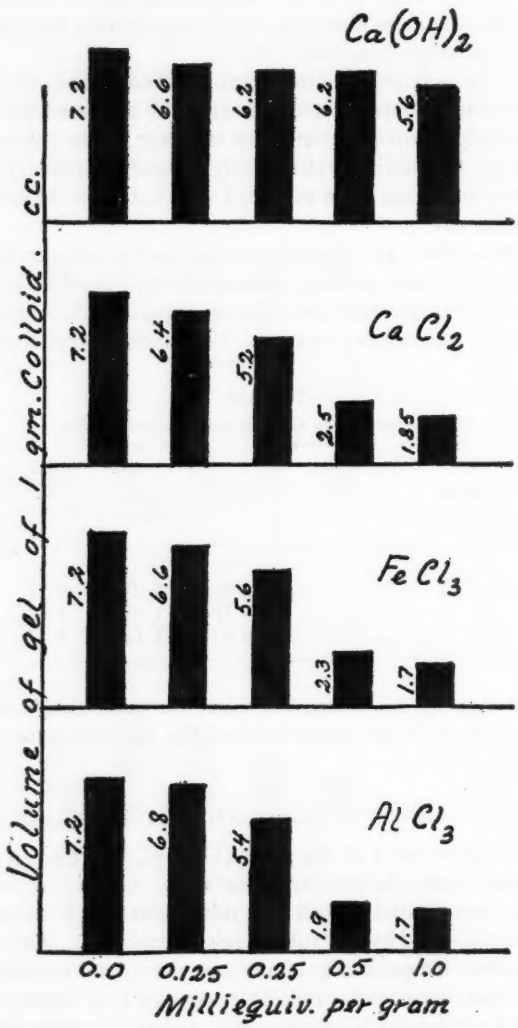


FIG. 19. THE SUPPRESSION OF THE SWELLING OF Na-SATURATED SHARKEY COLLOID BY VARIOUS ELECTROLYTES

tion of the colloid. (Their linkage to the silicate valences may, however, be unlocked by hydrolysis in an alkaline medium.) We would therefore expect the greatest suppression of the swelling as a result of displacing the Na ions

by Al and Fe ions. The Al ions should be the most efficient ones because we have seen that this ion causes the greatest decrease in the exchange capacity, the Fe combination being too readily hydrolyzed (13).

Figure 19 shows the suppression of the swelling of the Na-saturated Sharkey colloid by the addition of $Ca(OH)_2$, $CaCl_2$, $FeCl_3$, and $AlCl_3$ at the rate of 0.125, 0.25, 0.05, and 1.0 m.e. per gram colloid. Comparing the effect of the three chlorides we note that $CaCl_2$ causes a slightly greater suppression in the two lowest concentrations. If these differences are real they may be accounted for by the practically complete hydroxidation of the first small quantities of $AlCl_3$ and $FeCl_3$ by the alkali-saturated colloid. Where 0.5 m.e. of the chlorides is added we find the following suppression of the swelling

$$Al > Fe > Ca$$

Where 1.0 m.e. is added per gram colloid the swelling is suppressed to 1.7 cc. by Al and Fe and to 1.85 cc. by Ca. This represents, however, no exact measure of the true osmotic imbibition because the colloid plus the capillary water will occupy a certain irreducible volume. The osmotic imbibition may therefore be less than indicated by the smallest volume of the gels.

It is important to note that $Ca(OH)_2$, in the proportions used, caused a far smaller suppression of the swelling than do the chlorides. The $Ca(OH)_2$-treated colloid contains excess base and has an alkaline reaction. But after the $Ca(OH)_2$ was added to the Na-saturated colloid the latter was exposed to the air during the drying. The hydroxides, $Ca(OH)_2$ and NaOH (the latter formed by displacement), must therefore be largely converted into carbonates. The $CaCO_3$, being only slightly soluble, does not appreciably suppress the swelling as a free electrolyte, and because of the low Ca ion concentration in the solution there will be only a moderate displacement of the Na ions in the complex. The result is that the complex remains highly saturated with sodium and retains therefore to a great extent its capacity to swell. This emphasizes the fact long recognized that lime is not the proper agent to be used for improving the condition of alkali soils.

RELATION BETWEEN PRESSURE AND WATER CONTENT

If a suspension of a soil colloid is placed on a filter sufficiently fine to retain the particles, a certain amount of the water will be removed by gravity while another portion of the water will be retained by the colloid. The quantity of water thus retained will depend upon the cation exchange capacity of the colloid and upon the nature of the displaceable cations. The quantity of water retained by the colloid will also be affected by the presence of electrolytes and by the valence of the ions as demanded by the Donnan equation (12). A bentonite, which has an exchange capacity of about 1 m.e. per gram retains in the Na-saturated condition, nearly 9.5 cc. of water per gram solid material. At this water content the suspension has already assumed the consistency of a gel. This is remarkable in view of the fact that the solid phase (sp. gr. = 2.65)

occupies only about one twenty-fifth of the volume of the gel. If spherical particles of uniform size are assumed their distance apart would be nearly four times their radius.

The water which is removed by gravity represents the free, outside or intermicellar solution whereas the water which is retained within gel constitutes the micellar solution. The latter is more or less rigidly held by the osmotic force created by the micellar ion atmosphere. When the free, intermicellar solution is removed the micelles come into intimate contact and are no longer free to move about. In place of a viscous fluid there results, therefore, a more or less rigid gel.

TABLE 89

Quantities of water, in cubic centimeter per gram oven-dry (110°C.) material, retained by bentonite gel against different pressures

PRESSURE, P	WATER, w	$w \cdot \sqrt[3]{P}$	$\frac{r_1 - r}{r}$	$\left(\frac{r_1 - r}{r}\right) \cdot \sqrt[6]{P}$
cm. Hg	*cc.*			
0.2	9.36	5.52	1.97	1.52
1.2	7.16	7.62	1.72	1.77
5.6	5.93	10.55	1.56	2.09
10.5	4.94	10.82	1.42	2.10
13.8	4.38	10.51	1.34	2.08
20.5	3.95	10.81	1.26	2.08
30.0	3.37	10.49	1.16	2.05
41.0	3.14	10.86	1.11	2.06
50.0	2.96	10.95	1.07	2.06
61.0	2.71	10.70	1.02	2.03
70.0	2.57	10.62	0.99	2.01

To remove any part of the micellar solution, pressure must be applied and this pressure must be equal to the opposing osmotic pressure. In the first of this series of papers (12) it was shown that the ratio of $\frac{x}{y}$, that is, the Donnan distribution of the free electrolyte, increased rapidly with a decrease in the water content of the gel. This indicates a rapid increase in the micellar ion concentration (z) as we pass from the outermost to the innermost layers of the ion atmosphere. The pressures required to remove successive quantities of water from the gel should therefore increase in the same proportion and should represent the osmotic pressure at various "depths" in the micellar atmosphere.

In order to determine the relationship between the pressure and the water retained by the gel the following experiment was performed. A thick, yet fluid, suspension of bentonite containing 100 gm. solid matter in 1,500 cc. water was prepared. Portions of this suspension were placed in Büchner funnels with fused-in sintered filter discs of fine porocity. By means of a vacuum pump and a mercury manometer the pressure in the filter flasks was kept at

the desired point by frequent adjustment until no more water was removed from the gel. The water was caught in a narrow graduated test tube placed inside the flasks. Evaporation was prevented by covering the funnel with a rubber stopper into which a glass tube, drawn at the upper end into a very fine capillary, was inserted. The water remaining in the gel at the various pressures was determined by drying at 110°C.

The results are shown in table 89, in which the first column gives the pressures in centimeters of mercury. The second column gives the number of

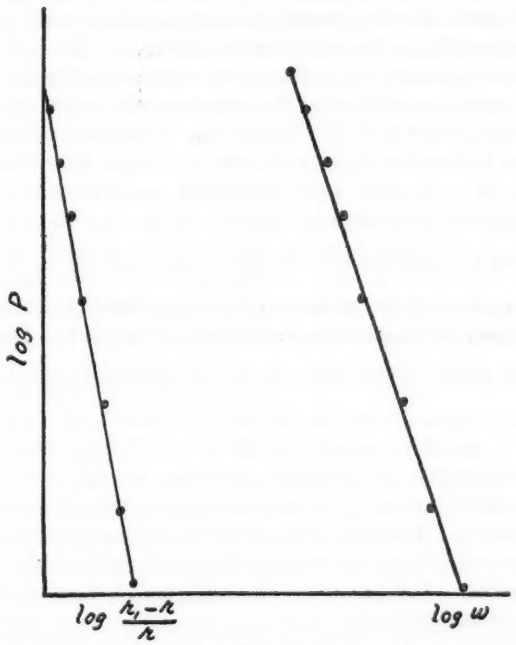


FIG. 20. THE RELATION BETWEEN THE VOLUME OF WATER (w) PER GRAM BENTONITE (ALSO BETWEEN THE THICKNESS OF THE WATER ENVELOPE OF THE PARTICLES, $\frac{r_1 - r}{r}$) AND THE PRESSURE (P) APPLIED

cc. of water retained by one gram oven-dry colloid. The third column gives the products of $w \cdot \sqrt[3]{P}$ where P = pressure and w = water as given in the preceding columns. The fourth column gives the thickness of the osmotically imbibed water envelope in terms of the radius r of the particles which are assumed to be spherical and of uniform size. These values are derived as follows: 1 gm. dry colloid, sp. gr. = 2.65, represents a solid sphere = 0.378 cc. with a radius r = 0.448 cm. The volume v of the gel is 0.378 + w cc.; r_1 is the radius of a sphere of volume v. The radius r_1 represents, therefore, the radius r

of the solid sphere plus the thickness of the water envelope which is $r_1 - r$. In terms of r as a unit of measure the thickness of the water envelope is $\frac{r_1 - r}{r}$. If now the individual particles were all spherical and of the same size this relationship would remain the same. Although this is only an approximation, it may be assumed that the ratio of the thickness of the water envelope at the various water contents to the "average effective radius" is very nearly proportional to the values in column four. The fifth column gives the product of the thickness of the water envelope and the sixth root of the pressure.

It will be noted that the pressure necessary to remove more water from the gel increases rapidly as the water content decreases. With the exception of the two lowest pressures the mathematical relationship is such that the cube root of the pressure multiplied by the water content is equal to a constant, the average value of which is 10.70. The increase in pressure is therefore inversely proportional to the cube of the water content. Since the volume of a sphere is proportional to the cube of the radius this would mean that the pressure increases inversely as the sixth power of the radius or as the sixth power of the distance from the solid surface. It will be seen that the $\frac{r_1 - r}{r}$ values when multiplied by the sixth root of the corresponding pressures yield approximately constant values, except, as before, in the case of the first two figures.

If log P is plotted against log w on the one hand and against log $\frac{r_1 - r}{r}$ on the other, as in figure 20, straight lines with a slope of 3 and 5.6 are respectively obtained. It should be pointed out that the cubes of the values $r_1 - r$, which represent the thickness of the water envelopes, are only approximately proportional to the volume of the water, the deviation becoming greater the lower the water content. The slope of the corresponding line is therefore less than 6.

The range over which this water and pressure relationship holds has not been determined. Equipment for this study is now being procured and the results will be reported later.

INTERNAL PRESSURE

At high water content of the gel, the product $w \cdot \sqrt[3]{P}$ decreases rapidly; the gel does not imbibe as much water as is demanded by the relationship. To explain this let us briefly review the theory of the imbibition. It is assumed that the force which opposes the applied pressure is (above a certain moisture content where water exists outside the range of molecular attraction), an osmotic force created by the ions dissociated by the colloidal particle. These ions tend to diffuse in all directions but are held in check by the electrostatic attraction of the oppositely charged colloidal ion complex which forms the nucleus of the ion atmosphere. It is this attraction which limits the swelling or osmotic imbibition, which would otherwise take place until the osmotic pressure was the same throughout the system, that is, until the distribution of the

ions was equalized. The electrostatic restraint upon the diffusion of the dissociated ions constitutes therefore an internal pressure which acts in opposition to the osmotic pressure. This internal pressure appears to equal about 1.5 cm. of mercury or about 0.02 of an atmosphere as determined by extrapolation of $w \cdot \sqrt[3]{P} = K$.

It will be recalled (12) that by applying the osmotic equation $2y + z - 2x = e$ to the distribution of ions between the inside and outside solution of a bentonite gel after complete imbibition of NaCl solutions the value of e was nearly constant in all cases and equal to a concentration of about 0.0008 molar (compare table 3). This corresponds to about 0.02 of an atmosphere, which is the same as here estimated from the water content-pressure relationship. There exists therefore at equilibrium a residual osmotic pressure which is unable to cause a further imbibition of water. If there were no opposing force the gel would swell until $e = 0$. But this would lead to an equal distribution of the micellar ions and to their separation from the colloidal ion complex. This is, however, prevented by the electrostatic attraction which reaches a critical maximum when the micellar ions have diffused out into the surrounding medium a certain average distance. An equilibrium is then established and the gel will swell no more. It is significant that this theoretical deduction is supported by two so different experimental methods which both yield the same approximate values in terms of osmotic pressure. In its electrical equivalent this internal pressure expresses itself in the potential difference of the double layer, that is, the electrokinetic potential.

DEPRESSION OF THE FREEZING POINT

Bouyoucos (3) found that the depression of the freezing point of soils increased in a geometric progression whereas the percentage of water decreased in an arithmetric progression. If we plot the logarithms of the depressions against the logarithms of the water content per gram soil as reported by Bouyoucos we get approximately a straight line with a slope not very different from that of the corresponding graph in figure 20. This is exactly what we should predict on the basis of the theory here presented. But Bouyoucos gives another interpretation. He does not recognize the existence of a micellar ion atmosphere but believes that the depression of the freezing point is entirely due to the soluble electrolytes of the soil. To explain the geometric instead of an arithmetric progression of the depression he assumes that a portion of the water held by soils is unfree or unavailable to act as a solvent. Thus if 15 per cent water is rendered inactive as a solvent by a clay, then at 40 per cent moisture content there would be 25 per cent available, and at 20 per cent moisture content only 5 per cent would be available to dissolve the salts. The soil solution would then be five times instead of twice as concentrated at the lower moisture content.

This view, which has been adopted by some investigators, is, in the author's opinion, unsatisfactory. If the molecularly attracted water cannot act as a

solvent how then can we account for the almost instantaneous reaction of soils with ions as in base exchange reactions? Bouyoucos' assumption might be tested in several ways. If his explanation is correct there should be no increase in the depression if, as in our present experiments, the various moisture contents were arrived at by withdrawal of the solution by pressure instead of adding decreasing amounts of water to the dry soil as was done. Secondly an electrodialyzed soil free from diffusible electrolytes might be used. In either case our present theory would demand a geometric progression in the increase of the freezing point depression.

It is true that the hypothesis of Bouyoucos would account for the "negative adsorption" which we have here explained on the basis of the Donnan distribution. But it will not account for the valence effect nor for the effect of the concentration of the free electrolyte unless we make the very improbable assumption that the quantity of "unfree" water varies accordingly. The fact that the "negative adsorption," the swelling, the quantities of water retained against various pressures, the viscosity (and, it might be predicted, the depression of the freezing point) are directly related to the quantity and the nature of the diffusible ions in combination with the colloid indicates that all these phenomena, and many others, are *functions of a colloidal ionogen*. The hydration of the ions, on the basis of which some investigators would account for the lyophillic behavior of colloids, is here held to exert an indirect effect in that the most highly hydrated ions undergo the highest degree of dissociation by the complex. The effect of the concentration and valence of added electrolytes upon these functions can be satisfactorily accounted for only by the Donnan equilibrium.

THE COMPOSITION OF THE MICELLAR SOLUTION

We have seen that the micellar solution must be less concentrated with respect to free electrolytes than the outside or intermicellar solution. This enables us to make some very interesting predictions which have in part been verified and which are in part under investigation.

The first deduction is that if, by pressure, we remove the micellar liquid from a fully imbibed colloid, in equilibrium with the outside solution, we shall find the concentration (y) of the expressed solution lower than the concentration (x) of the (outside) solution which runs off under the influence of gravity alone. Further, if the micellar ion concentration (z) increases rapidly in the direction of the interface then the concentration of the ions of the free electrolyte will decrease in the same direction. The expressed solution should therefore become more and more dilute as we increase the pressure.

We may choose any ion and, if it be the H ion, we should find an increase in pH of the expressed liquid as the pressure is increased.[2] This will at first sight

[2] This is true only as far as free acid is present. If the medium is alkaline the pH of the expressed liquid must decrease. The same distribution law holds of course for the H^+ and OH^- ions of the water as well as for any extraneous ions, but since $[H^+]\cdot[OH^-] = K_w$ the dissociation of the water will be affected by removal of the latter from the micellar solution.

seem like a paradox, for we have long known that a moist *negative colloid* or its suspension reacts more acid than its extract. Figure 21 will, however, serve to explain the apparent contradiction. It represents a section (*a*) of a particle, (*b*) of the micellar solution, and (*c*) of the outside solution. The complex exists partly in combination with H ions which undergo a certain degree of dissociation, diffuse into the micellar solution, and establish a concentration gradient indicated by the size of the letter *z*. In the solution there are also a certain number of free H ions which are paired with diffusible anions. At equilibrium the equation

$$x^2 = y\,(y + z)$$

must be satisfied no matter which part of the system we consider. Where *z* is larger *y* must be smaller. The *y* concentrations must therefore grow smaller, as indicated by the size of the letter *y* in the figure.

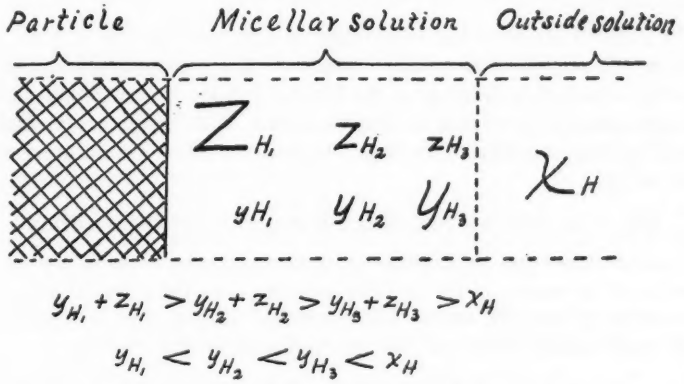


FIG. 21. THE SCHEMATIC REPRESENTATION OF THE INCREASE IN THE CONCENTRATION OF THE IONS DISSOCIATED BY THE COLLOID (*z*) AND THE DECREASE IN THE CONCENTRATION OF THE FREE IONS OF THE SOLUTION (*y*), IN THE DIRECTION OF THE SURFACE OF THE PARTICLES

Now, it is obvious that

$$y_{H_1} + z_{H_1} > y_{H_2} + z_{H_2} > y_{H_3} + z_{H_3} > x_H;$$

hence the H ion concentration of the suspension or the gel must be higher than that of the filtrate or of the outside solution.

It is also obvious that

$$y_{H_1} < y_{H_2} < y_{H_3} < x_H$$

hence if, by means of increasing pressure, we extract successive portions of the micellar liquid we should find a progressive decrease in the H-ion concentration. The H ions belonging to the micelle are obviously not removable.

As shown in a previous publication (13) in the case of *electropositive colloids*, in which the micellar atmosphere consists of anions, the suspension or the moist gel must react less acid than its extract, but here again the concentration of any ion in the expressed liquid should become smaller at high pressures.

The solution removed from the slightly acidified bentonite gel was found to have a higher pH the higher the pressure, a difference of about 0.2 pH being observed between the solution run off by gravity as compared to the solution obtained in the pressure range between 60 and 70 cm. of mercury. When the bentonite was suspended in a 0.02 *N* NaCl solution instead of water it was found that while the solution which ran off by gravity alone had a concentration of 0.0231 *N*. the latter was reduced to 0.0220 *N*. in the fraction extracted in the pressure range between 60 and 70 cm. of mercury. While this supports the theory it shows that marked differences in concentration are to be expected only at higher pressures. Apparatus permitting an investigation at very much higher pressures are now procured. The results of this work will be reported later.

The author's attention has been called to a recent paper by McCool and Youden (10) which is of the greatest importance to our present subject. They report a considerable decrease in the H- and PO_4-ion concentrations of the solutions removed from peat at high pressures. No definite explanation is offered but they promise to continue the research, which should prove very illuminating.

THE P. D. BETWEEN THE MICELLAR AND THE OUTSIDE SOLUTION

If our postulate that the micellar ion concentration increases rapidly in the direction of the surface of the particles is correct then the potential difference between the gel and the outside solution should show an inverse relationship to the water content of the gel. By the Nernst equation the P.D. is

$$\frac{R\,T}{F}\,ln\,\frac{(y+z)}{x} = \frac{R\,T}{F}\,ln\,\frac{x}{y}$$

The test might meet with difficulties but an attempt to investigate this relationship is now being inaugurated. The plan is to work with the following chain: calomel electrode-saturated KCl—outside equilibrium solution—gel at various water content—saturated KCl—calomel electrode.

DISCUSSION AND SUMMARY

The subject might be briefly recapilulated by the following statements:

The combined or constitutional water represents the internal water of the material in combination with the individual molecules in the form of hydrous oxides of silicon, aluminum, iron, and their combinations.

The molecularly attracted water is represented by the hygroscopic moisture. This water is held by powerful forces which are manifest by the heat of wetting and by a contraction of volume. This water exists in a very thin film which

apparently does not exceed 4 or 5 $\mu\mu$ in thickness, which corresponds to the range of molecular attraction. The quantity of water thus adsorbed by the soil is a function of the surface and is independent of the nature and quantity of exchangeable cations. Where a relationship between the heat of wetting on the one side and the composition and exchange capacity on the other side was observed it must be remembered that the particle size and hence the surface varied accordingly (2). The lower heat of wetting reported by Pate (17) for Na-saturated colloids may be ascribed to the slowness with which such materials wet.

Soil colloids imbibe greatly varying quantities of water depending upon:

(a) their composition or more directly upon their exchange capacity;
(b) the nature of the exchangeable cations;
(c) the charge of the particles;
(d) the position of their isoelectric point if amphoteric or
(e) their ultimate pH, i.e., the strength of their acid group;
(f) the concentration of free electrolytes and the valence of the ions, both according to the Donnan equilibrium.

This imbibition is obviously therefore a function of an ionic condition of the colloid, in other words, of a colloidal ionogen. It is an osmotic imbibition brought about by the dissociation of diffusible ions by the colloidal particle. This forms the colloidal micelle consisting of the particle, the ion atmosphere, and the osmotically imbibed water.

The relationship between the applied pressure and the water content indicates that the concentration of the micellar ions increases rapidly in the direction of the surface. This theory leads to the following deductions:

The free electrolyte must be more concentrated in the outside than in the inside or micellar solution. The pH of a negative suspension must be lower than that of its extract.

The pH of a positive suspension must be higher than that of its extract.

The concentration of any ion in the solution removed from a colloid at high pressures must be lower than its concentration in the solution filtered off without pressure.

The potential difference between the gel and its extract must increase as the water content of the gel decreases.

Some of these deductions have been verified.

REFERENCES

(1) ANDERSON, M. S. 1924 The heat of wetting of soil colloids. *Jour. Agr. Res.* 28: 927–935.

(2) ANDERSON, M. S., AND MATTSON, SANTE 1926 Properties of the colloidal soil material. U. S. Dept. Agr. Bul. 1452.

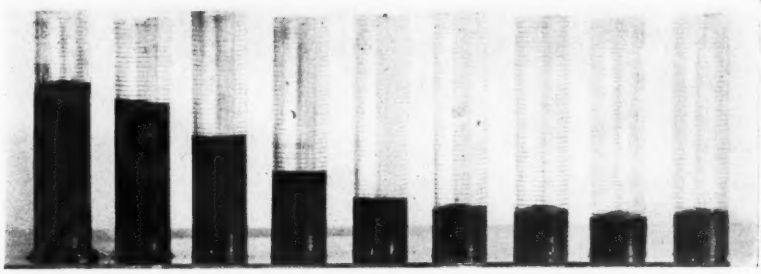
(3) BOUYOUCOS, G. J. 1916 Further studies on the freezing point lowering of soils. Mich. Agr. Exp. Sta. Tech. Bul. 31.

(4) BOUYOUCOS, G. J. 1917 Classification and measurement of the different forms of water in the soil by means of the dilatometer method. Mich. Agr. Exp. Sta. Tech. Bul. 36.

(5) EDSER, E. 1922 Molecular structure and the physical properties of liquids. *Brit. Assoc. Adv. Sci. Rpt.* 1922: 40–114.
(6) EHRENBERG, PAUL 1922 Die Bodenkolloide, ed. 3. Dresden u. Leipzig.
(7) GEDROIZ, K. K. 1929 Der adsorbierende Bodenkomplex. Dresden u. Leipzig.
(8) HARKINS, W. D., AND EWING, D. T. 1921 A high pressure due to adsorption, and the density and volume relations of charcoal. *Jour. Amer. Chem. Soc.* 43: 1787–1802.
(9) LEBEDEFF, A. F. 1927 Methods of determining the maximum molecular moisture holding capacity of soils. *Proc. First Internatl. Cong. Soil Sci.* 1: 551–563.
(10) MCCOOL, M. M., AND YOUDEN, W. J. 1931 The pH and the phosphorus content of the expressed liquids from soils and plant tissues. *Contrib. Boyce Thompson Inst.* 3 (2): 267–276.
(11) MATTSON, SANTE 1927 The influence of the exchangeable bases on the colloidal behavior of soil materials. *Proc. First Internatl. Cong. Soil Sci.* 2: 185–198.
(12) MATTSON, SANTE 1929 The laws of soil colloidal behavior: I. *Soil Sci.* 28: 179–220.
(13) MATTSON, SANTE 1931 The laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311–331.
(14) MATTSON, SANTE 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 343–365.
(15) MITSCHERLICH, A. 1901 Untersuchungen über die physikalischen Bodeneigenschaften. *Landw. Jahrb.* 30: 361–445.
(16) MITSCHERLICH, A. 1920 Bodenkunde für Land und Forstwirte, ed: 3, Berlin.
(17) PATE, W. W. 1925 The influence of the amount and nature of the replaceable base upon the heat of wetting of soils and soil colloids. *Soil Sci.* 20: 329.
(18) ROBINSON, W. O., AND HOLMES, R. S. 1924 The chemical composition of soil colloids. U. S. Dept. Agr. Bul. 1311.
(19) RODEWALD, H. 1897 Thermodynamik der Quellung mit spezieller Anwendung auf die Stärke und deren Molekular-gewichtsbestimmung. *Ztschr. Phys. Chem.* 24: 193–220.
(20) RÜCKER, A. W., AND REINOLD, A. W. 1886 *Phil. Trans.* 177: 627 (Quoted from H. S. Taylor's Treatise on Physical Chemistry, p. 124, New York, 1925).

PLATE 1

INFLUENCE OF Na AND Ca UPON THE SWELLING OF THE SHARKEY SOIL COLLOID



Na.	100	75	50	40	30	20	10	5	0
Ca.	0	25	50	60	70	80	90	95	100
cc.	7.20	6.50	5.08	3.20	2.30	2.10	2.00	1.95	1.86